Westfälische Wilhelms-Universität Münster

Ionic Liquid-based Electrolytes for Next Generation Batteries

Stefano Passerini
University of Muenster, Institute of Physical Chemistry, Corrensstr. 28/30 Muenster
Germany

Beyond Lithium Ion, June 5, 2012

Muenster Electrochemical Energy Technology

Research Groups:

- **Prof. Martin Winter**
- **Prof. Stefano Passerini**

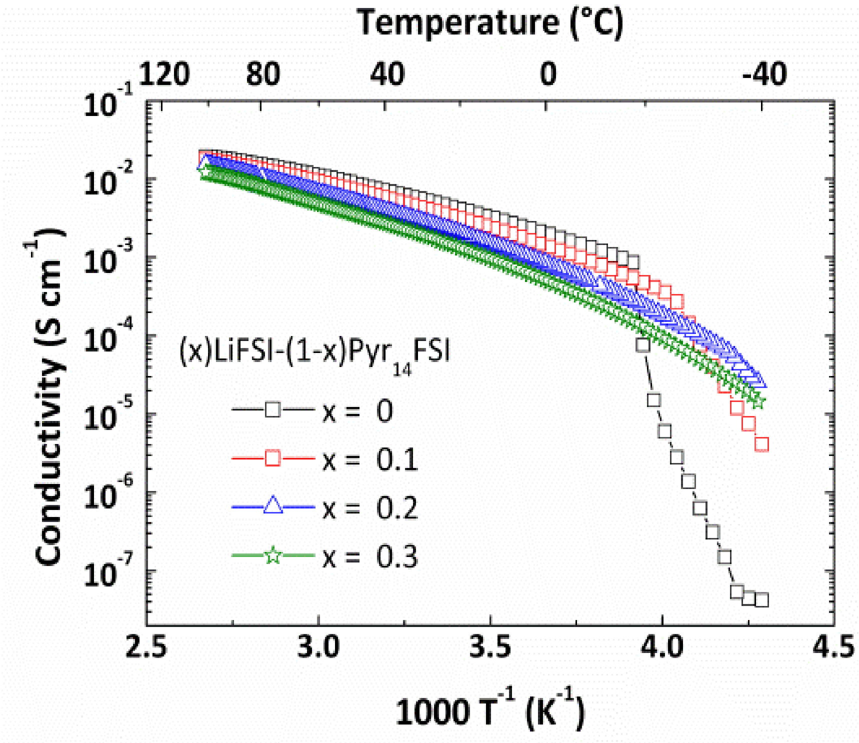
Young Researcher Groups:

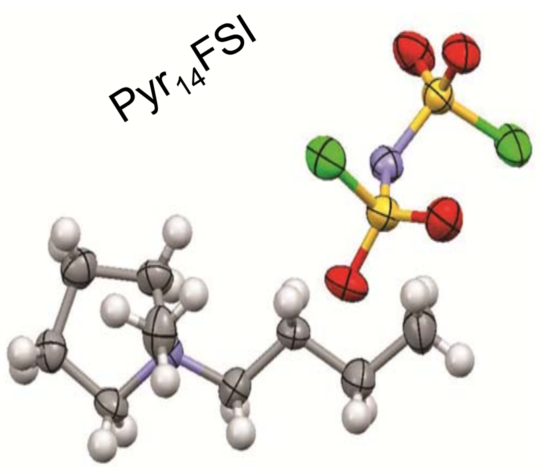
- **Dr. Alexandra Lex-Balducci** (2009 -)
- **Dr. Andrea Balducci** (2009 -)
- **Dr. Jie Li** (2012 -)

- **50 Ph.D. Students**
- **30 Scientists with Ph.D.**
- **10 Bachelor Students**

Ionic Conductivity in IL-based Materials for Energy Storage

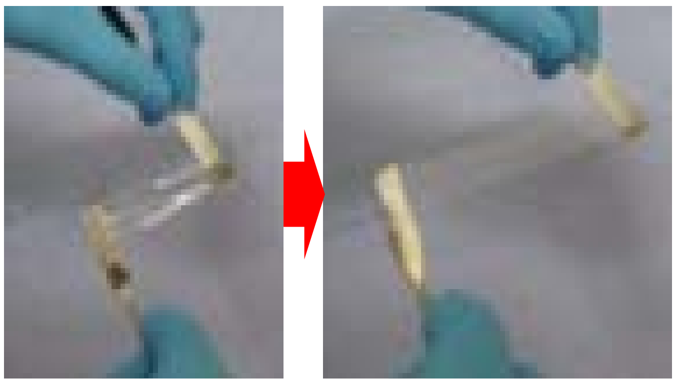
Liquid electrolytes

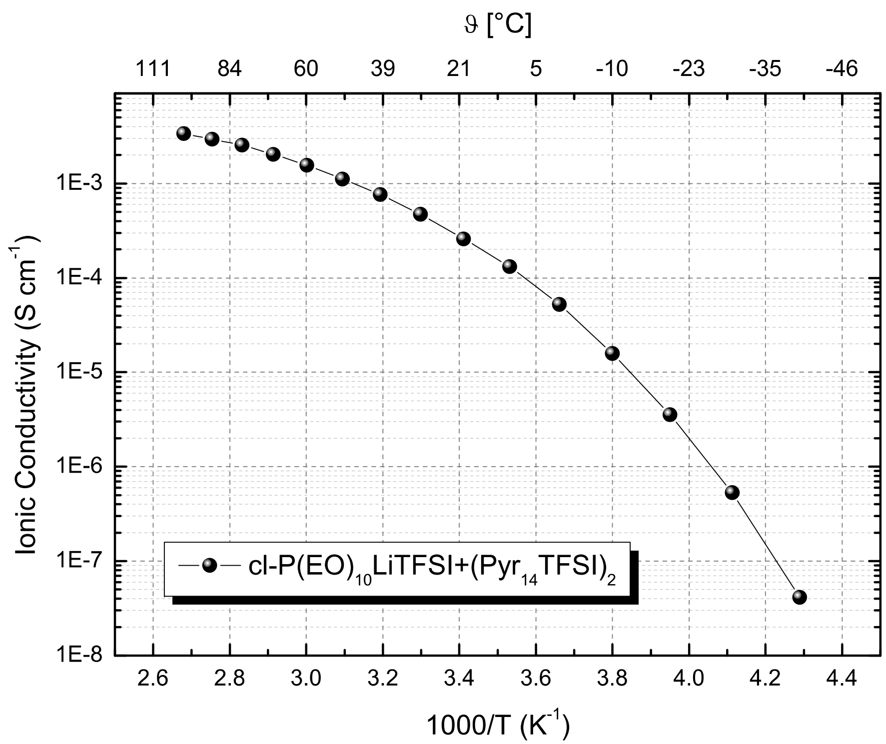




Ionic Conductivity in IL-based Materials for Energy Storage

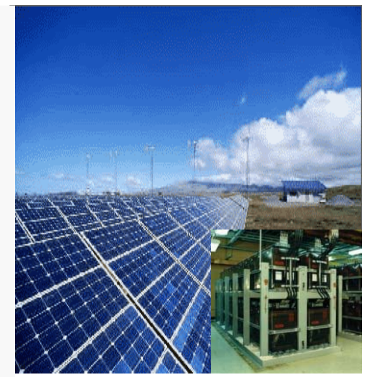
Polymer electrolytes





Li Ion Batteries Initiated a Technical Revolution....

… and might be ready for more



	Consumer Applications	LEV, Power Tools	Automotive HEV & EV	Stationary Elec. Storage
Market Size	€ 7Bio (2008)	medium € 0.7Bio (2008)	large € 25Bio (2020)	Very large
Market Introduction	1990 by Sony	2005	2012/15 (mostly HEV)	Realization has to be proven
Chances for Newcomers	Minimal	Moderate	(Very) Good	Depends on starting position
Typ. Battery-Size (kWh)	0.001 – 0.1	0.1 – 1	1 – 100	100 – 10.000

Key-role of Electrolyte in Li-Ion Batteries

Temperature range of use

Environment - friendly

Conductivity

Electrolyte System

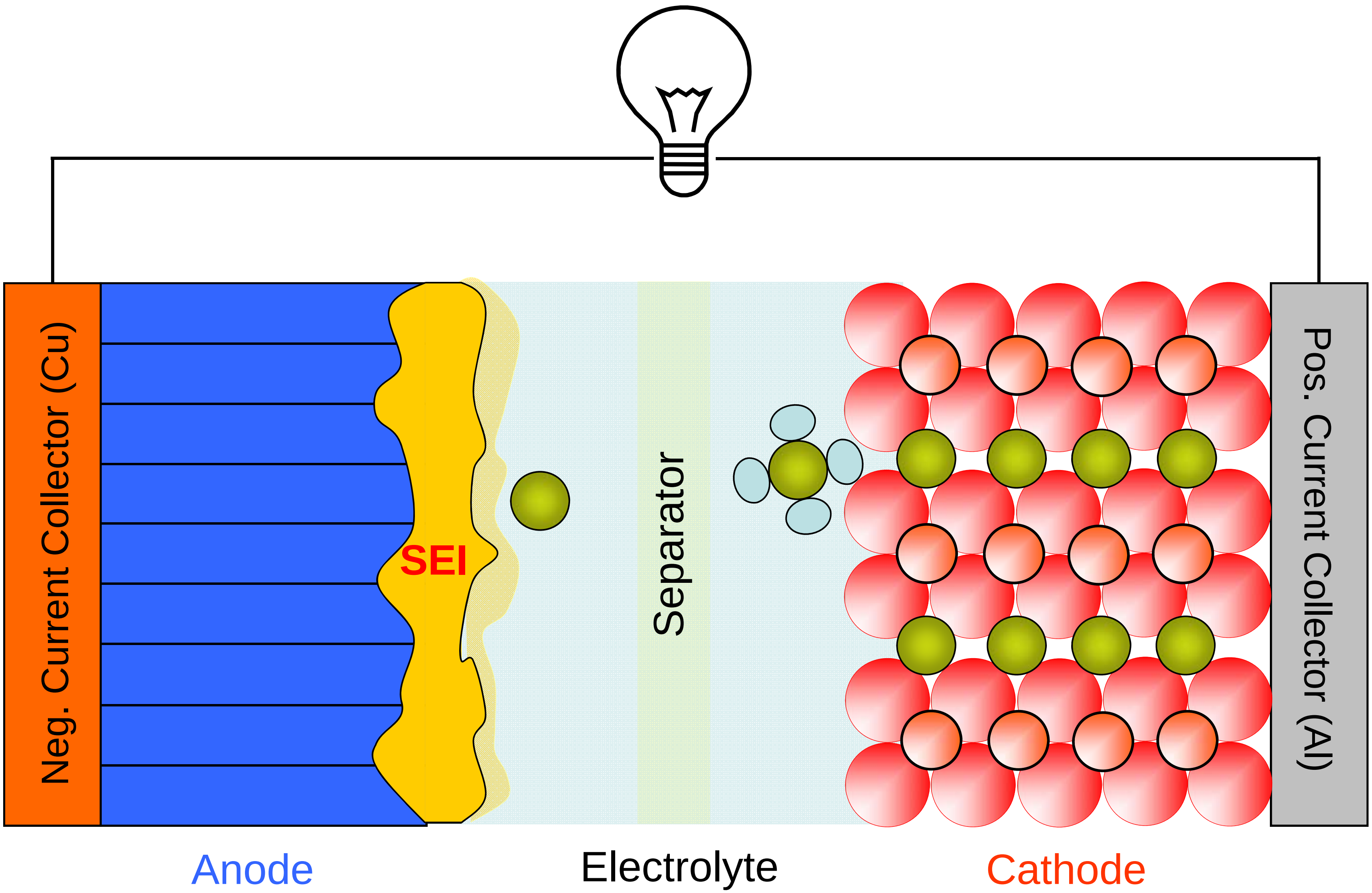
Vapor pressure

Film forming ability (SEI)

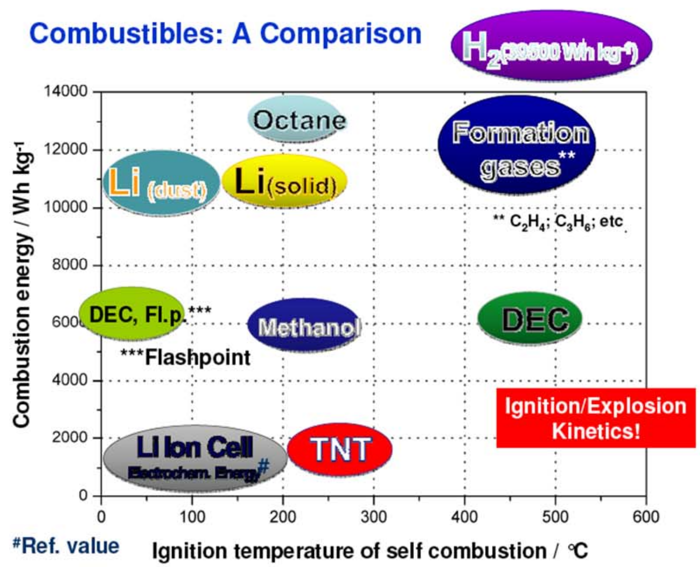
Electrochemical stability window

State of the art:
Organic solvent-based electrolytes
$LiPF_6$, EC, DEC, additives

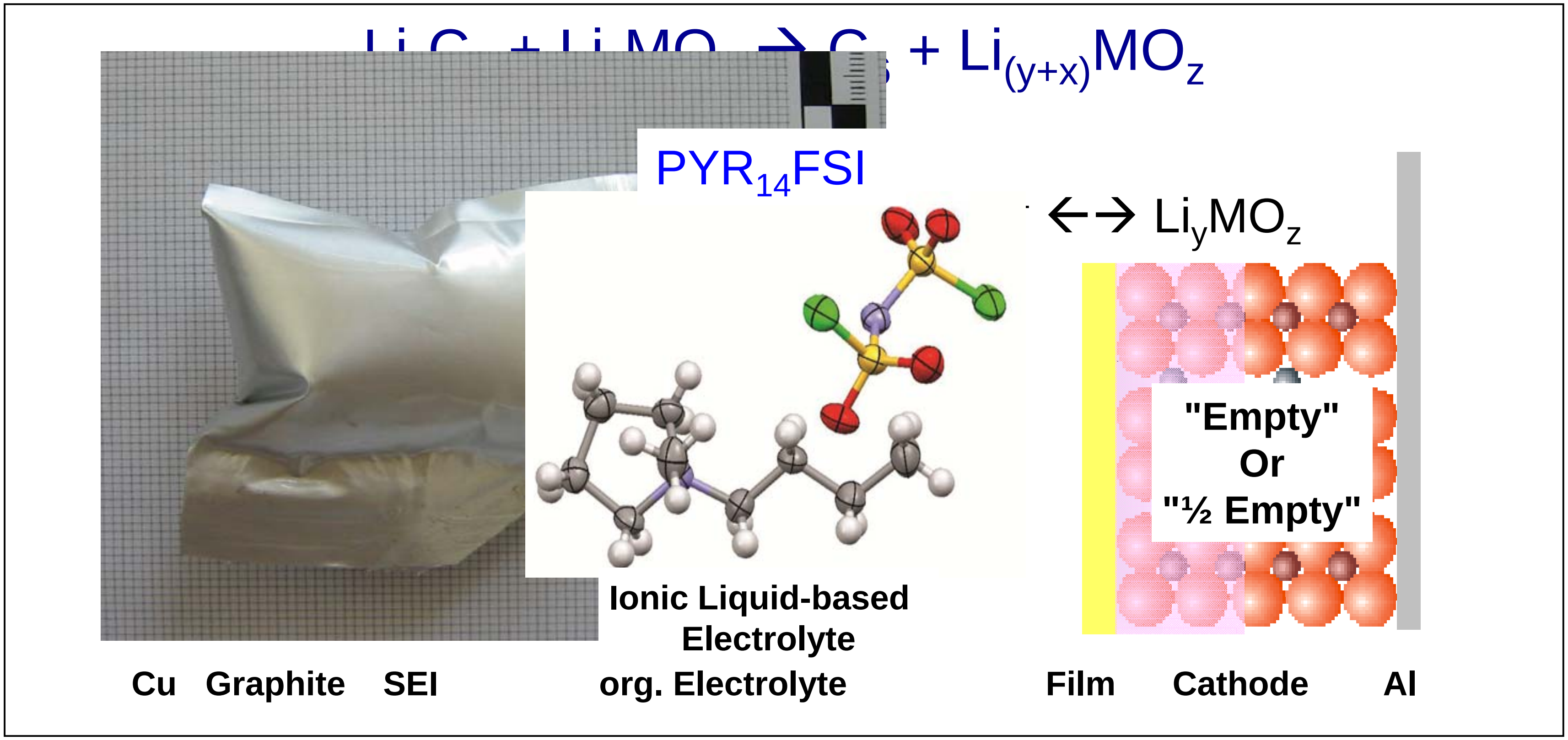
Li-Ion cells: Role of the SEI film



However …..
Safety of present Li-ion cells is still an open issue



Towards Safer Batteries:
What do we learn from LIBs?



Key Step Forward: Replacement of volatile, flammable and electrochemically unstable electrolyte components

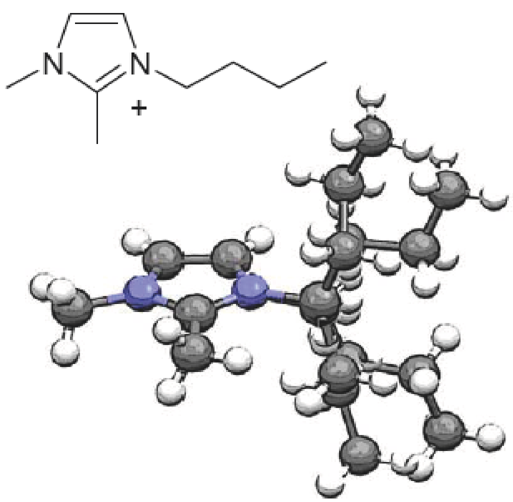
Room temperature molten salts (Ionic Liquids)

Ionic Liquids –Low Temperature Melting Salts

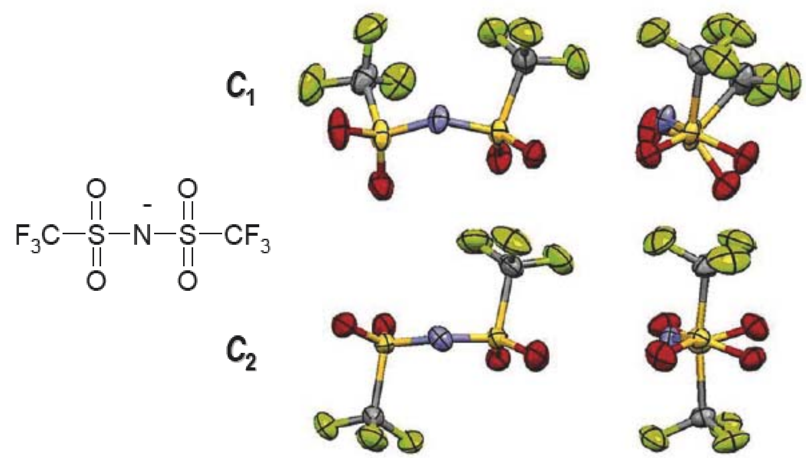
Salts, or mixtures of salts (composed solely of ions), which are liquid at low temperatures (< 100° C) – often below RT

Weak interactions due to large cation and anion delocalization <u>and</u> low tendency to crystallize due to flexibility (anion) and dissymmetry (cation)

Ion Conformational Changes



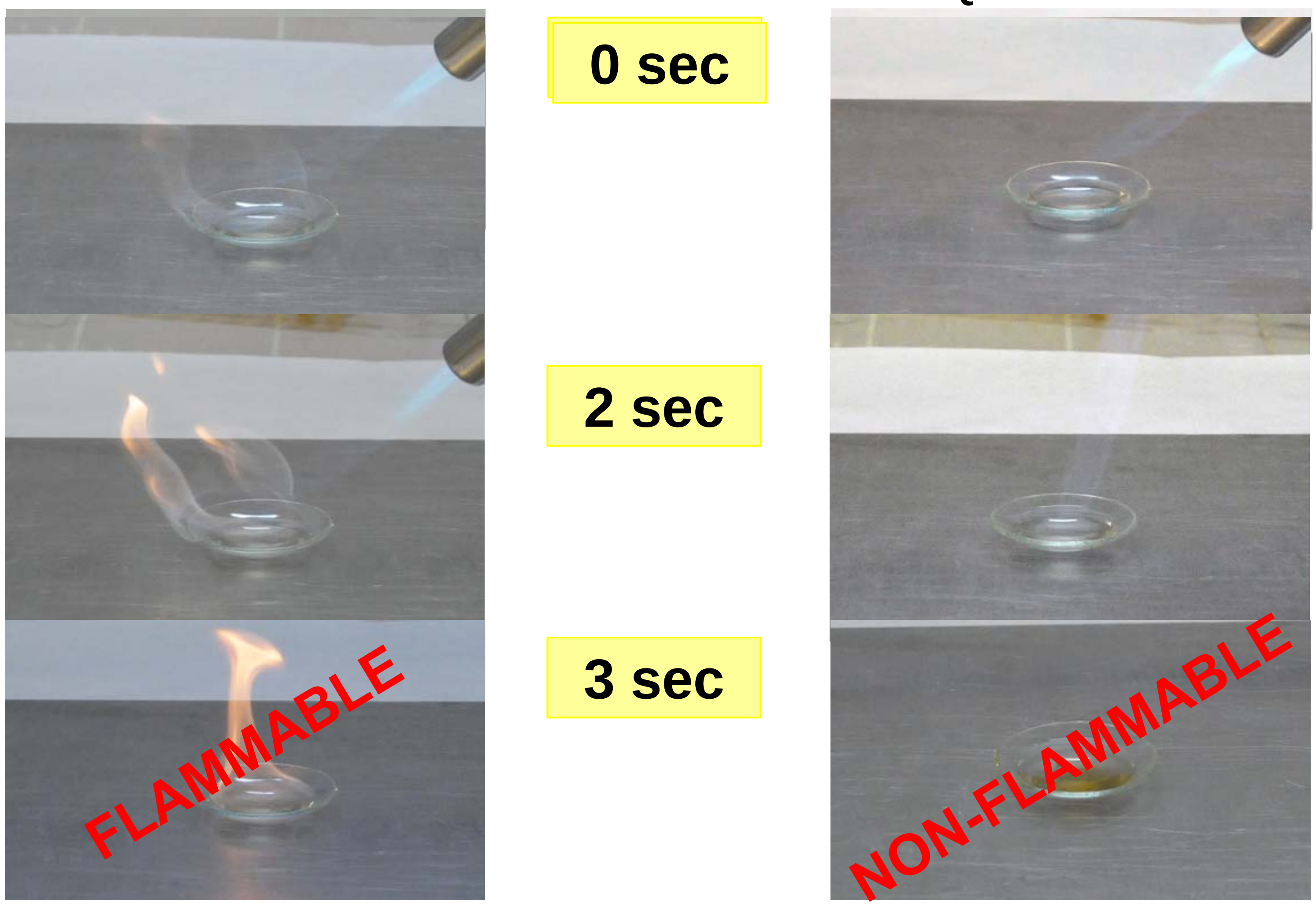
butyl conformations found in various crystal structures



well-know flexibility of the TFSI$^-$ anion between 2 low-energy conformations

Flammability: Organic electrolyte vs. Ionic Liquids

ORGANIC ELECTROLYTE **IONIC LIQUID ELECTROLYTE**



Ionic Liquids (IL, RTIL, RTMS, etc.)

Properties

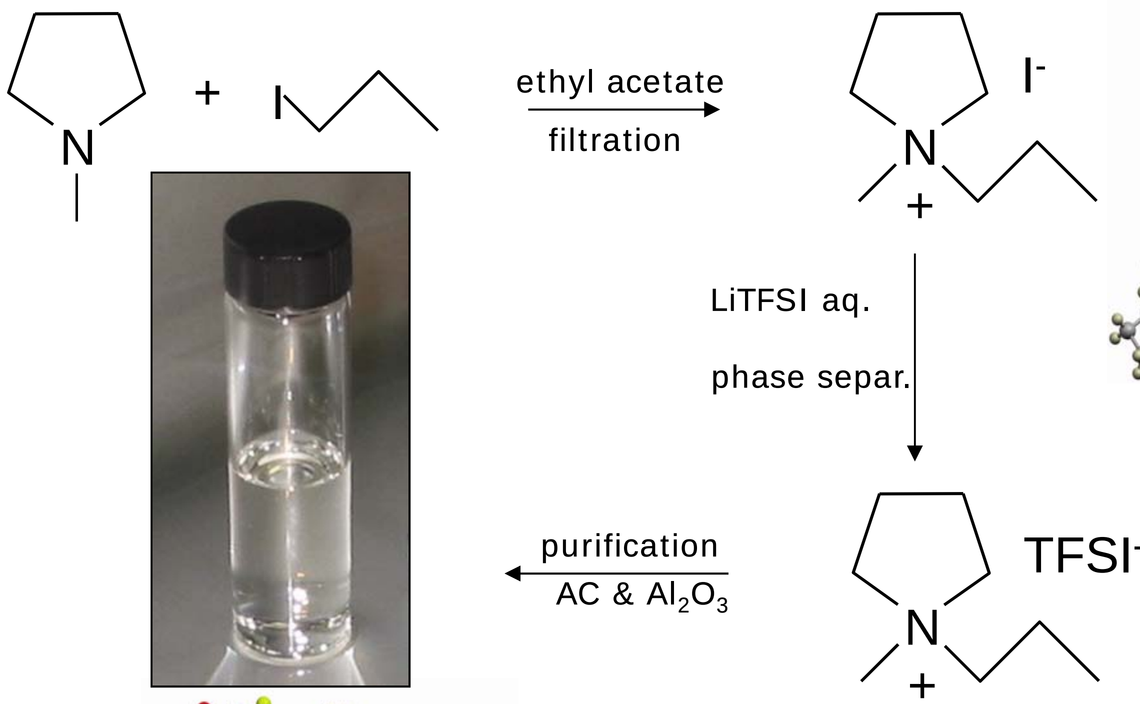
- Wide electrochemical window
- Wide liquid range
- Very low volatility at ambient pressure
- Good thermal stability
- High ionicity

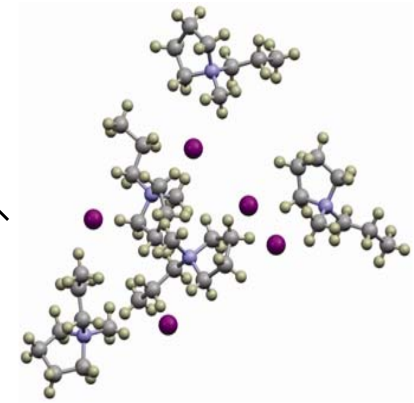
Solvents for liquid electrolytes

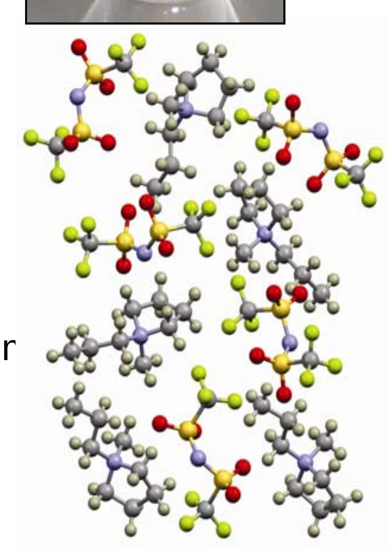
Co-salts for solid-state polymer electrolytes

Thousands of possible ILs available

Synthesis of Ionic Liquids







PYR$_{13}$TFSI ionic liquid

Impurities: < 100 ppr

Water: < 10 ppm

Clear, uncolored

Li = lithium

PYR$_{1A}$ = N-alkyl-N-methylpyrrolidinium

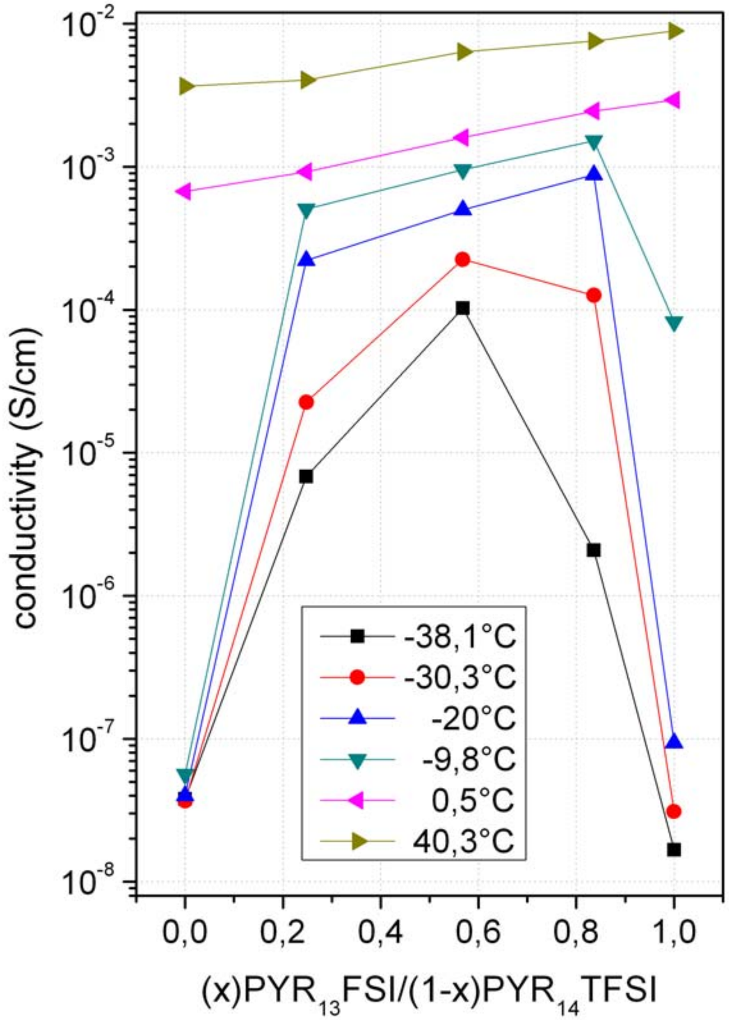
TFSI = bis(trifluoromethanesulfonyl)imide, $(CF_3SO_2)_2N^-$

FSI = bis(fluorosulfonyl)imide, $(FSO_2)_2N^-$

G.B Appetecchi et al., JES 153(9) (2006) A1685.

Combining Ionic Liquids → Boosting Performance

$PYR_{13}FSI$ (m.p. -10° C) - $PYR_{14}TFSI$ (m.p. -5° C)

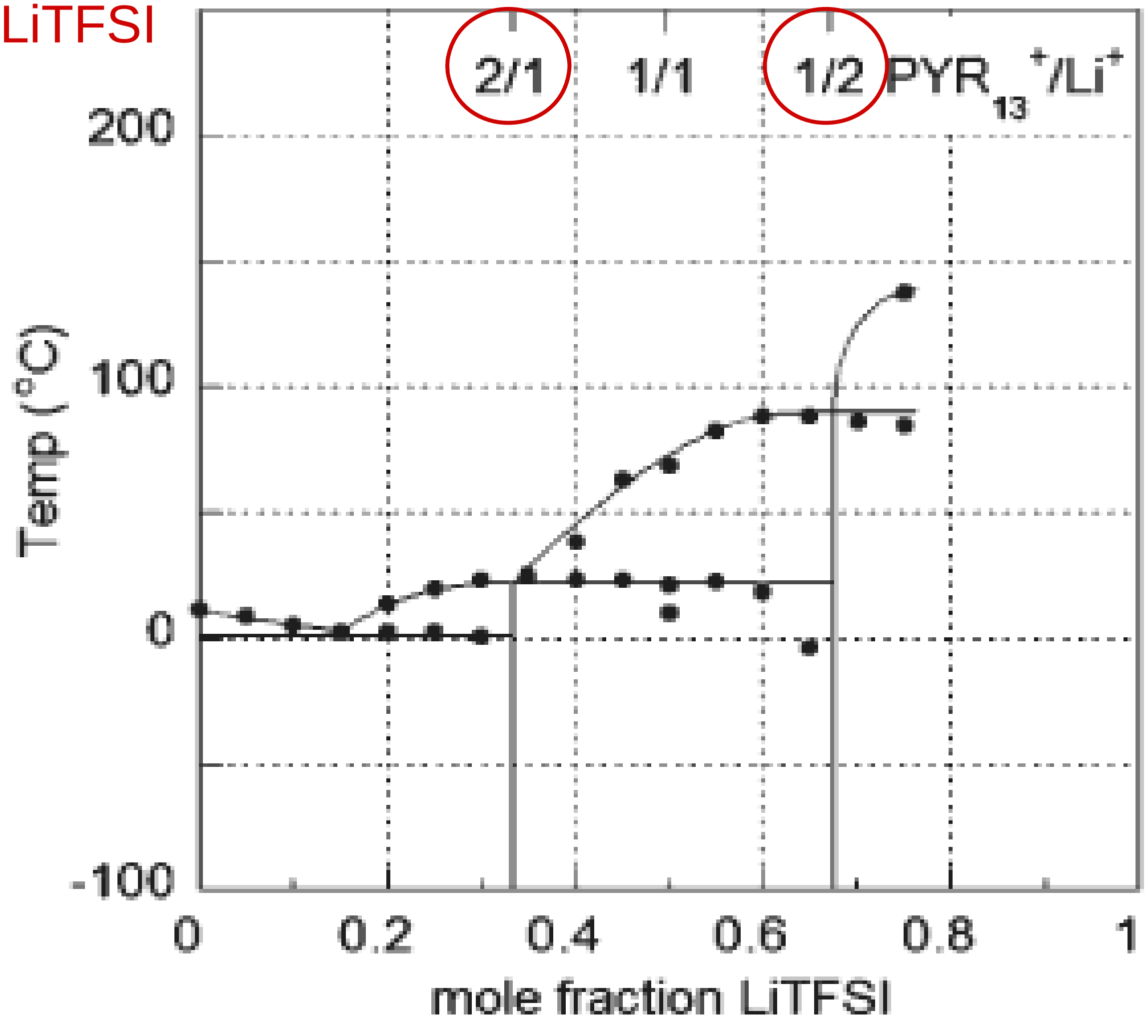


Mixtures have much lower melting temperatures than constituent Ionic Liquids due to additional ion mismatching

Castiglione et al. JPC B113, 10750 (2009), Zhou et al. JPC C 114, 6201 (2010), Kunze et al. JPC C 114, 12364 (2010)

Are ionic liquids capable of dissolving Li salts?

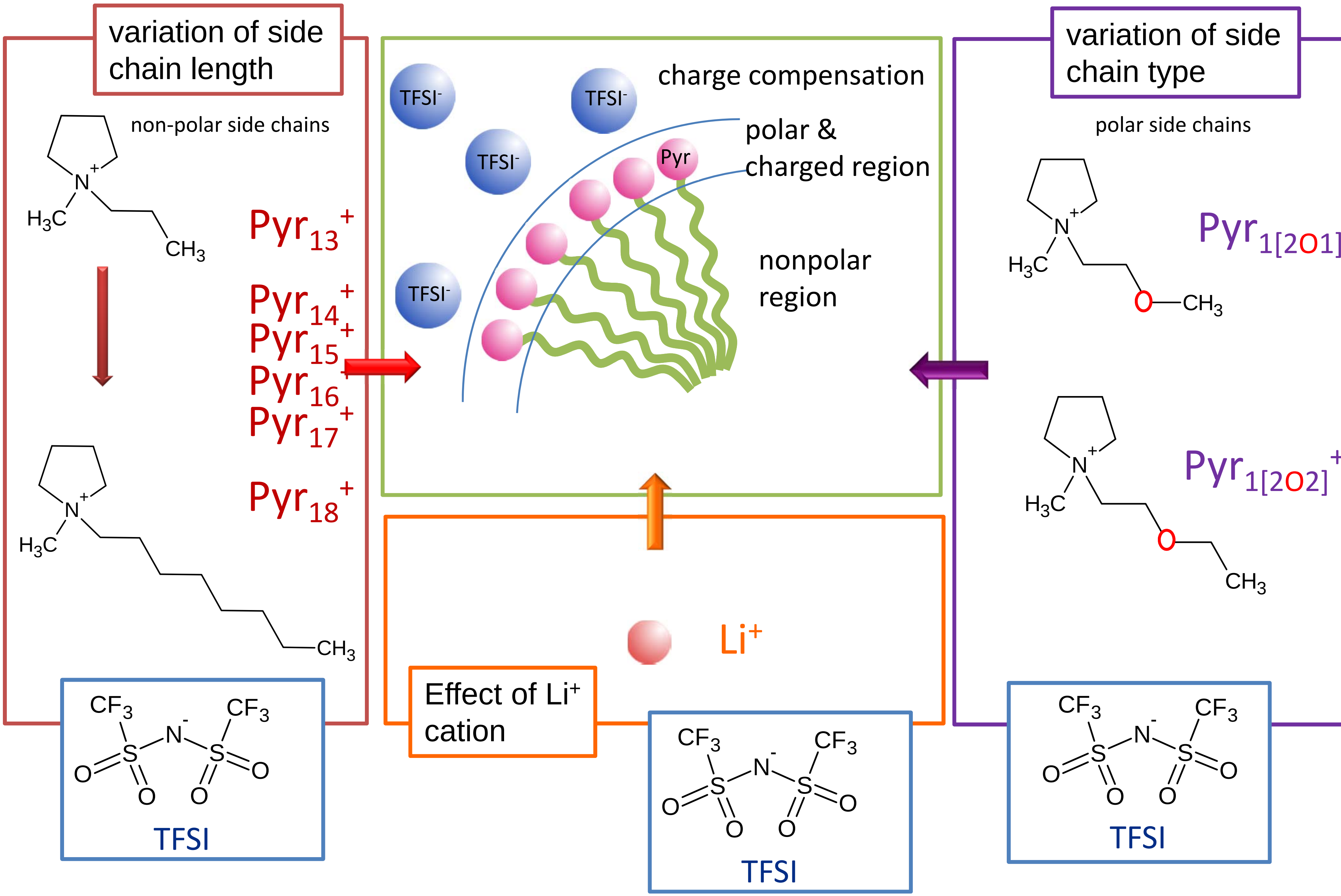
PYR$_{13}$TFSI - LiTFSI



Yes, but only at low Li concentration because new crystalline phases are formed for high Li content

Henderson et al. Chem. Mater. **16**, 2881 (2004)

Aggregation of Pyr_{1N}TFSI ILs (NMR, Raman)



Local Motion in Ionic Liquids: NMR characterization (Two Step Model)

spin-lattice and spin-spin relaxation of a surfactant are sensitive to fast local motions and slow motions, respectively

$\omega\tau_s >> 1$:

R_1 only influenced by fast bond rotations in the molecule that take place during the time τ_f – not influenced by aggregation of molecules

R_2 is largely influenced by the slow reorientations and experiences the molecular aggregation

spectral density:

$$J(\omega) = S^2 \frac{2\tau_s}{1+\omega^2\tau_s^2} + \left(1-S^2\right)\frac{2\tau_f}{1+\omega^2\tau_f^2}$$

$$S = \frac{\left(3\cos^2(\theta)-1\right)}{2}$$

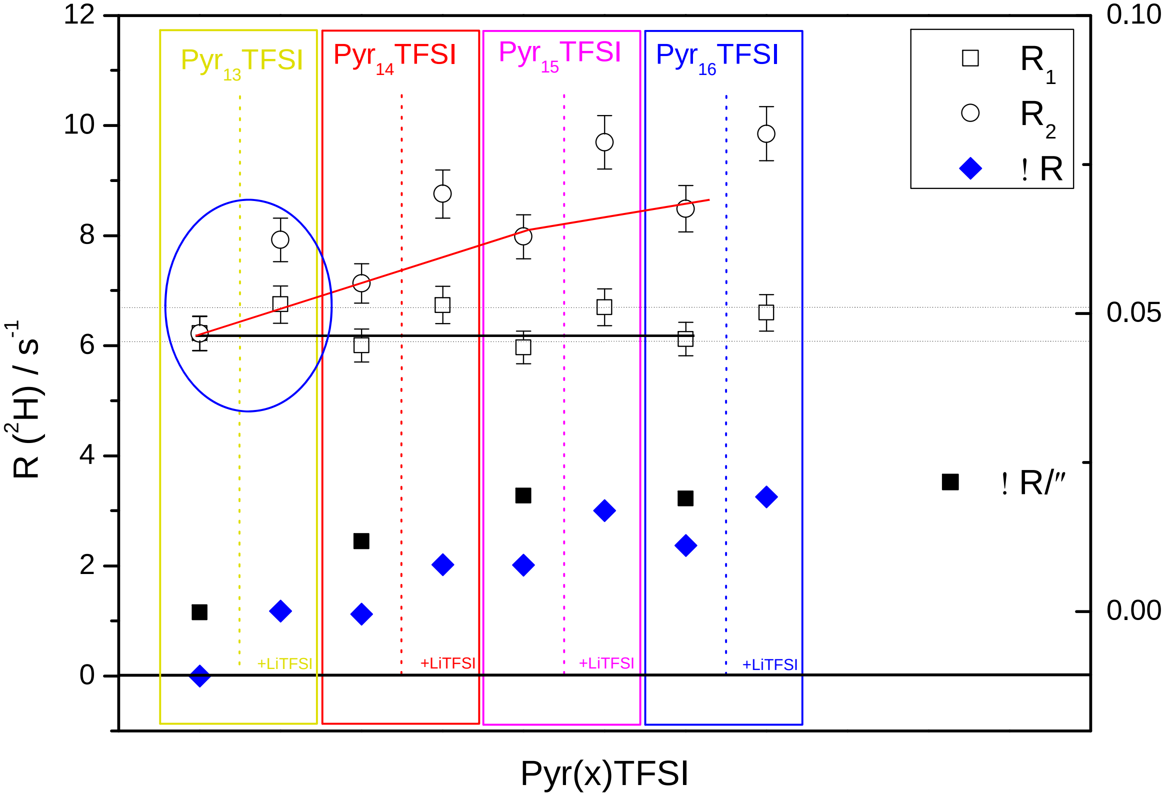
τ_f characterizes the fast internal motions (bond rotations)
τ_s describes rotational tumbling of the molecule

$$\Delta R = R_2 - R_1 \cong \frac{9\pi^2}{20}\chi^2 S^2 \tau_s$$

Wennerström, H., et al. *J. Am. Chem. Soc.* **101**, 6860-6864 (1979)

Aggregation in $Pyr_{1x}TFSI$

NMR measurements: T1 and T2 vs x (in $Pyr_{1x}TFSI$)



R_1 independent on chain length
⇨ fast local motions not influenced

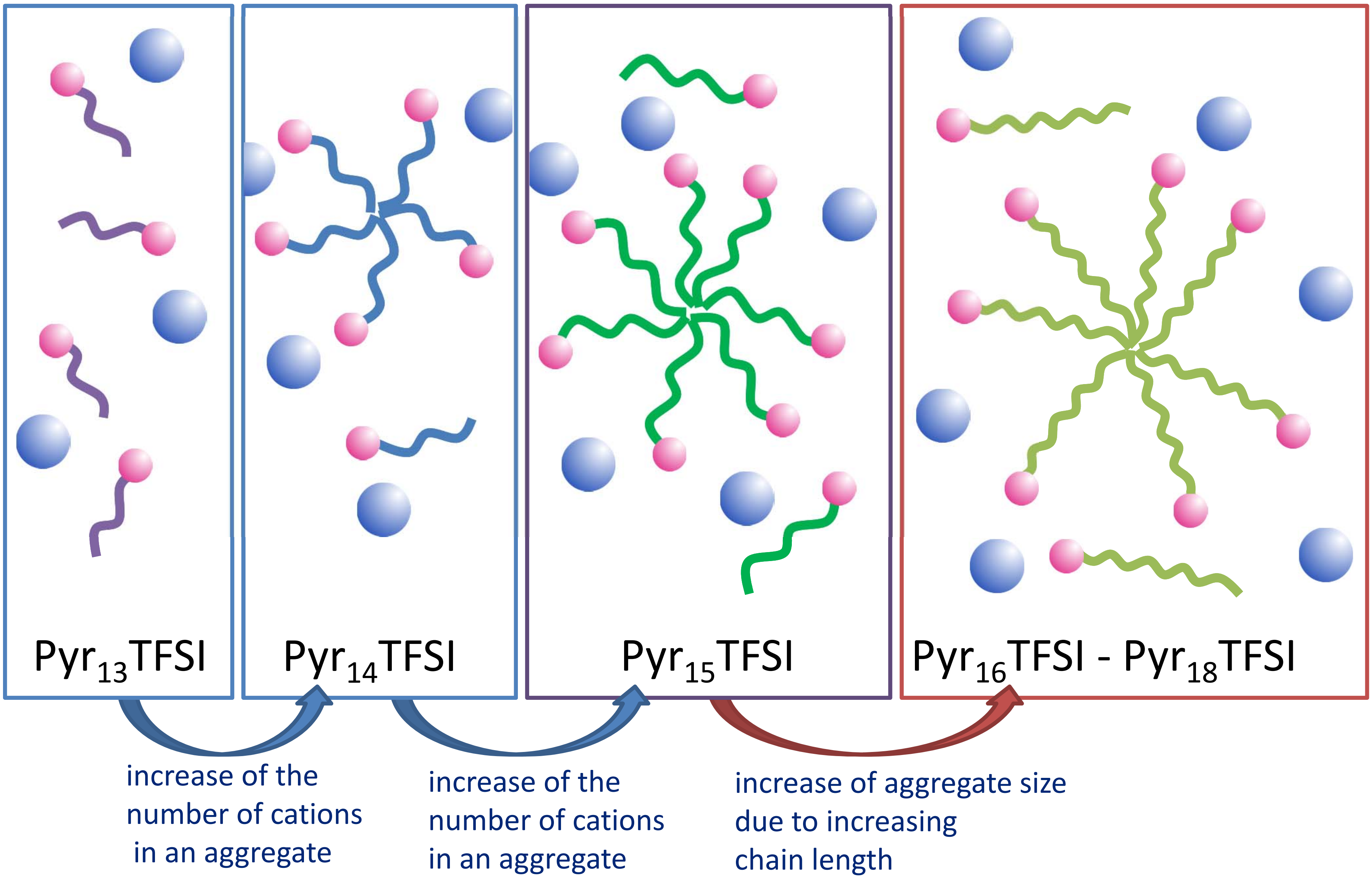
R_2 dependent on chain length
⇨ slow local motions influenced

two different linear dependences
⇨ different aggregation mechanisms

In presence of Li^+ ΔR differs from 0 already for propyl chain
⇨Li forces cation aggregation

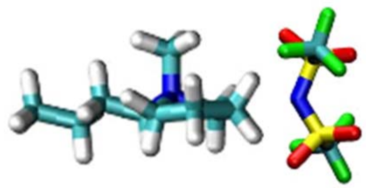
Typical behavior of micelles indicating the formation of aggregates

Aggregation type?

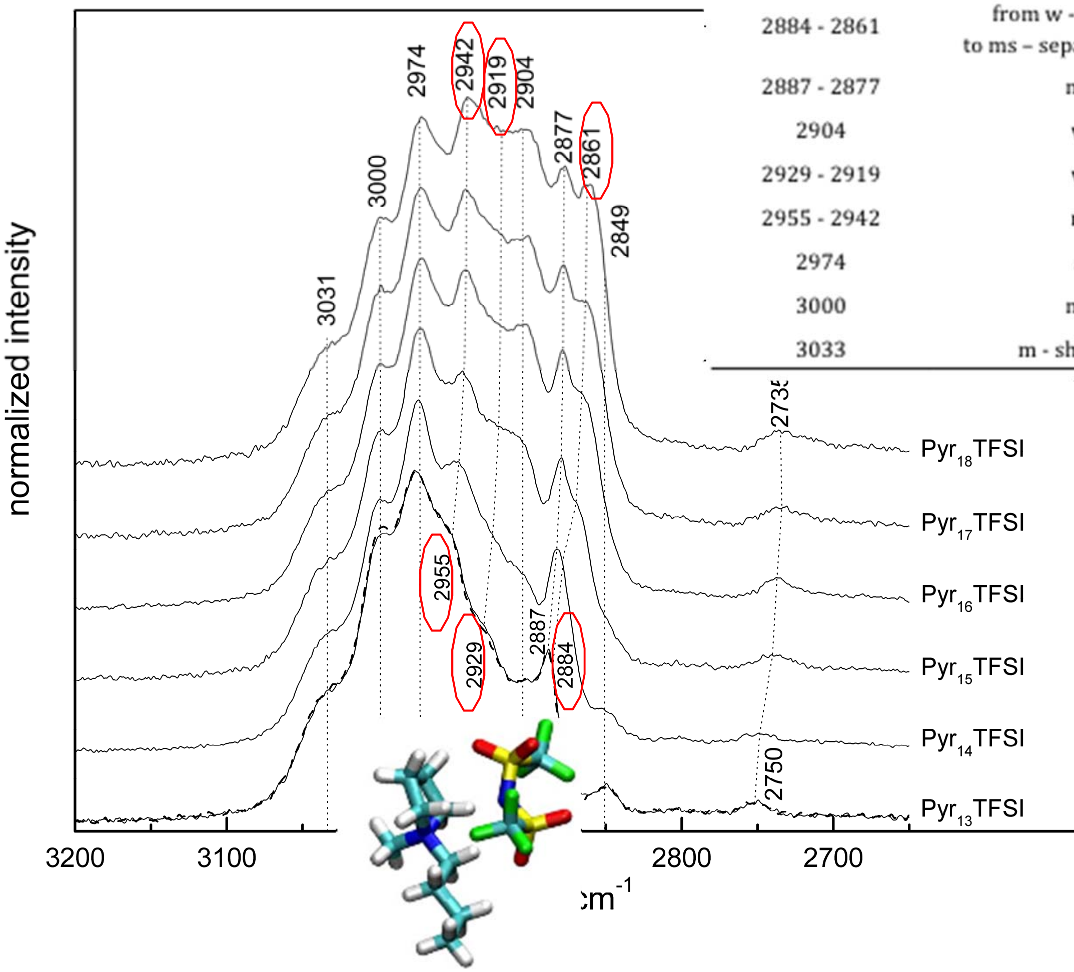


Aggregation in $Pyr_{1x}TFSI$

Raman measurements

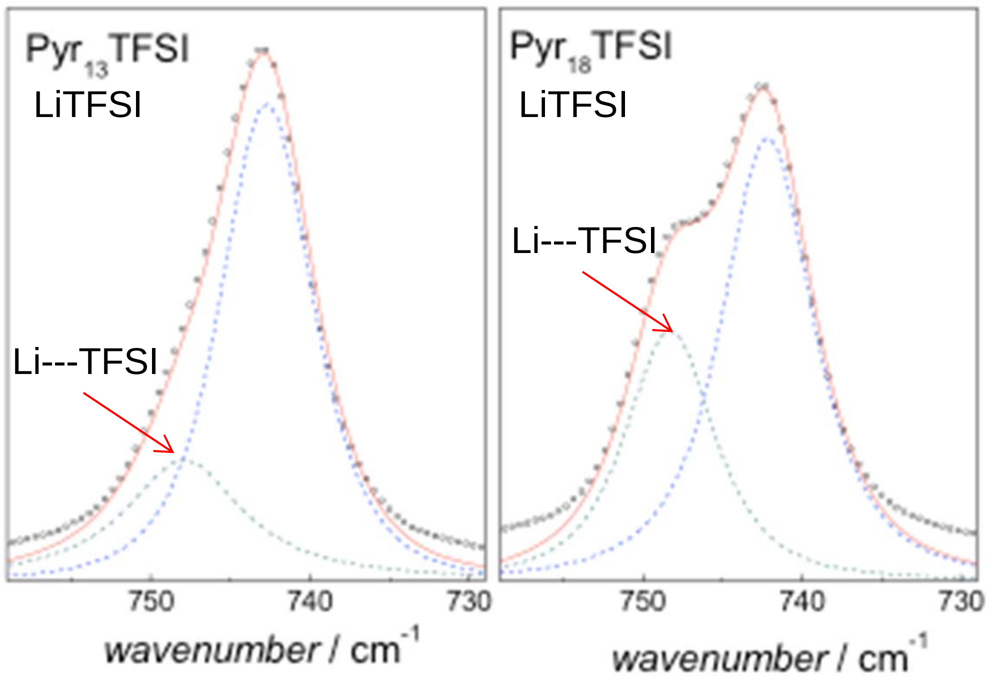


position / cm⁻¹	relative intensity	assignment
2750 - 2736	w	N^+–C_x shifting to lower wavenumbers with increasing side chain length x
2849	w	
2884 - 2861	from w - shoulder to ms – separated mode	
2887 - 2877	ms	–CH_2– in ring
2904	w	alkyl chain
2929 - 2919	w	–CH_2– in ring
2955 - 2942	m	–CH_2– in ring
2974	s	alkyl chain
3000	ms	ν_a(C–H) in C–CH_3
3033	m - shoulder	ν_a(C–H) in N^+–CH_3



The aggregation is confirmed by the shift of characteristic Raman peaks

Cation aggregation: Li^+ --- $TFSI^-$ ion-pairing



@ 742 cm^{-1} expansion and contraction of the whole TFSI-anion
@ 748 cm^{-1} damped TFSI-anion expansion and contraction due to Li^+ clustering

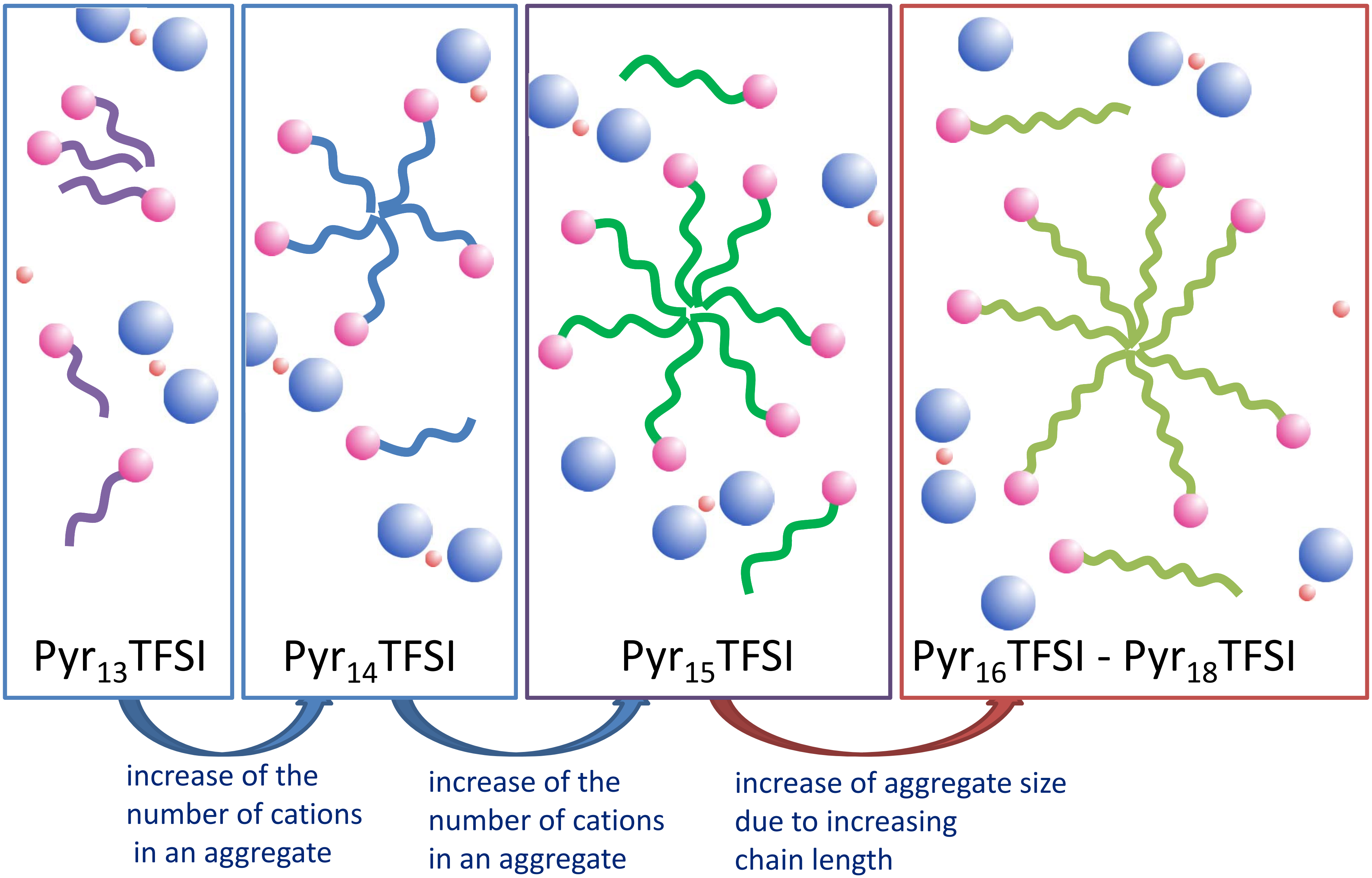
increase of mode @ 748 cm^{-1} with increasing side chain length
⇨ more anions are clustering the Li-cation when more Pyr-cations cluster with themselves

x in $Pyr_{1x}TFSI$	$[Pyr_{1x}TFSI]_{0.85}[LiTFSI]_{0.15}$		
	free TFSI position / cm^{-1}	Li^+····TFSI position / cm^{-1}	$n_{in\, Li^+ \cdots (TFSI^-)_n}$
3	742.7	747.9	1.90±0,01
4	742.3	748.3	2.12±0,01
5	742.4	748.1	2.34±0,01
6	742.2	748.3	2.33±0,02
7	742.2	748.3	2.34±0,02
8	742.2	748.3	2.33±0,02

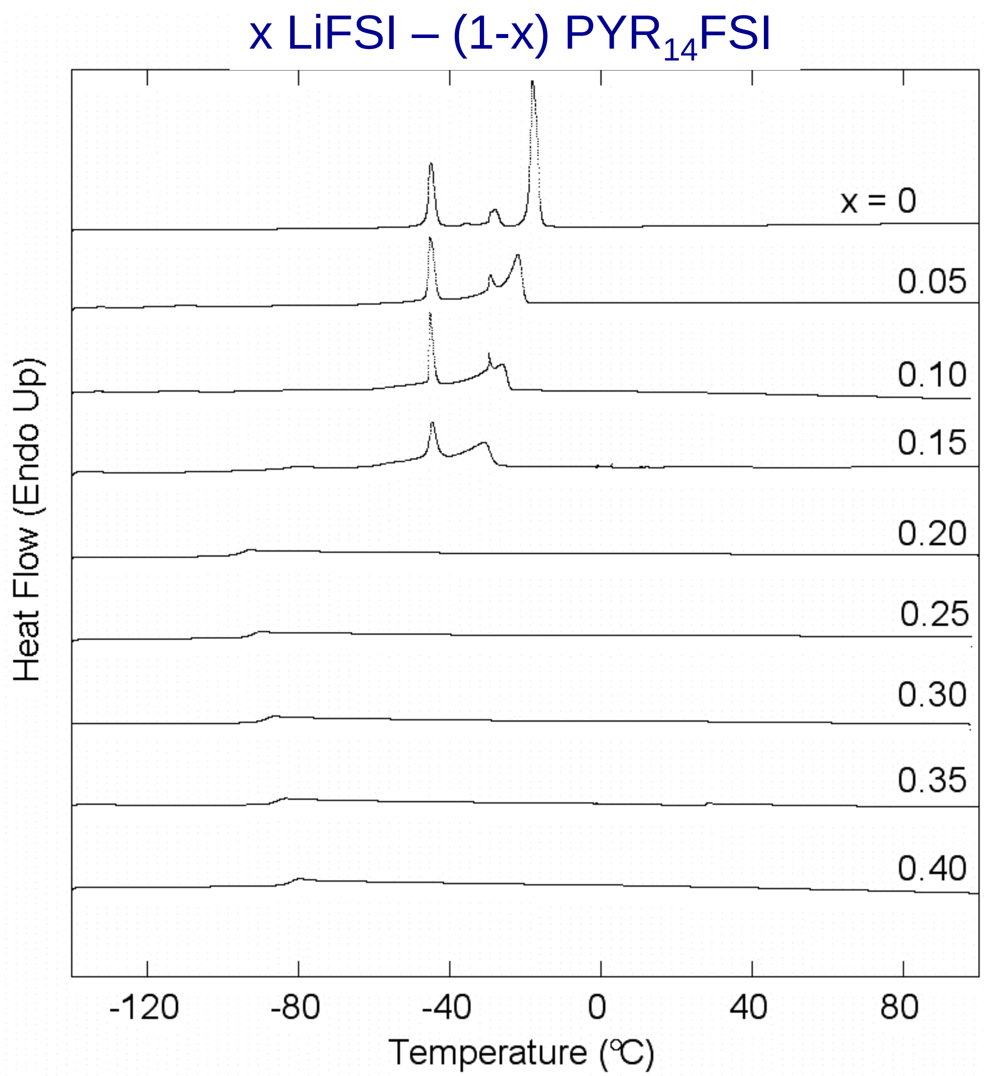
increase of anions, which surround the Li^+

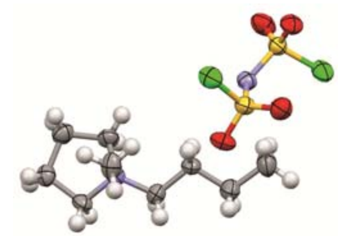
M. Kunze, et al., Adv. En. Mat. (2011) 1,1

PYR^{+}_{1x} aggregate formation in presence of Li^{+}



Tailored electrolyte: Li salt in $PYR_{14}FSI$





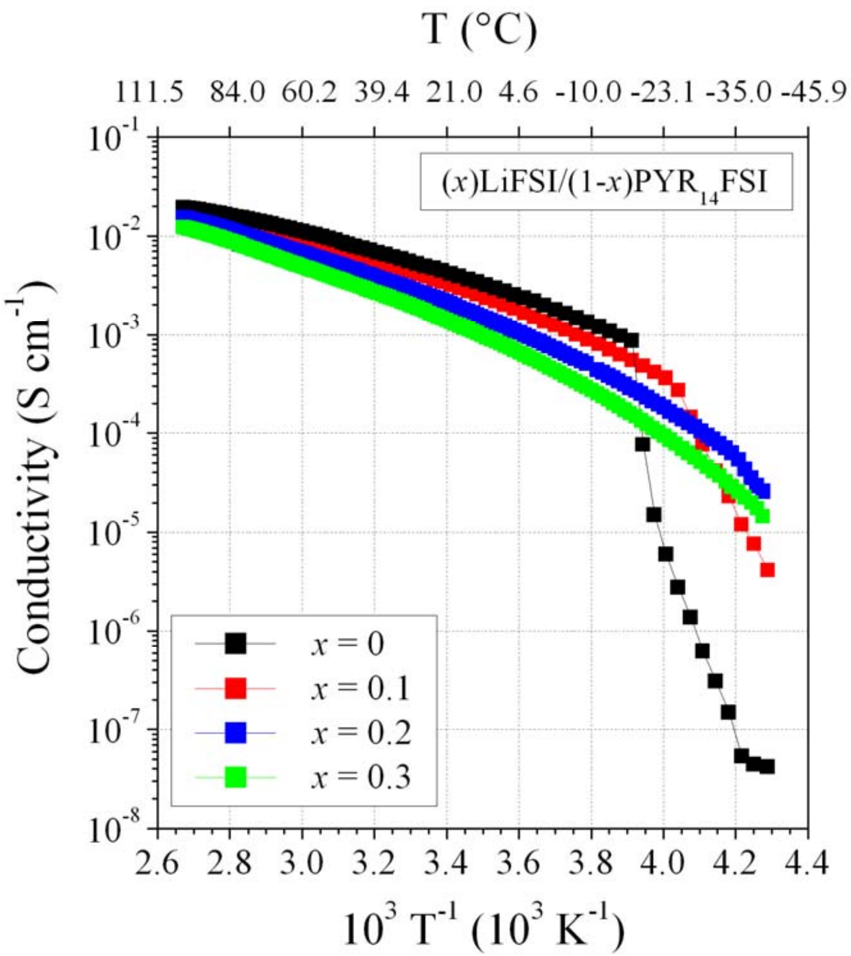
Sub-ambient temperature melting electrolytes

The electrolytic mixture 0.85 $PY_{14}FSI$ - 0.15 LiFSI melts below -40° C

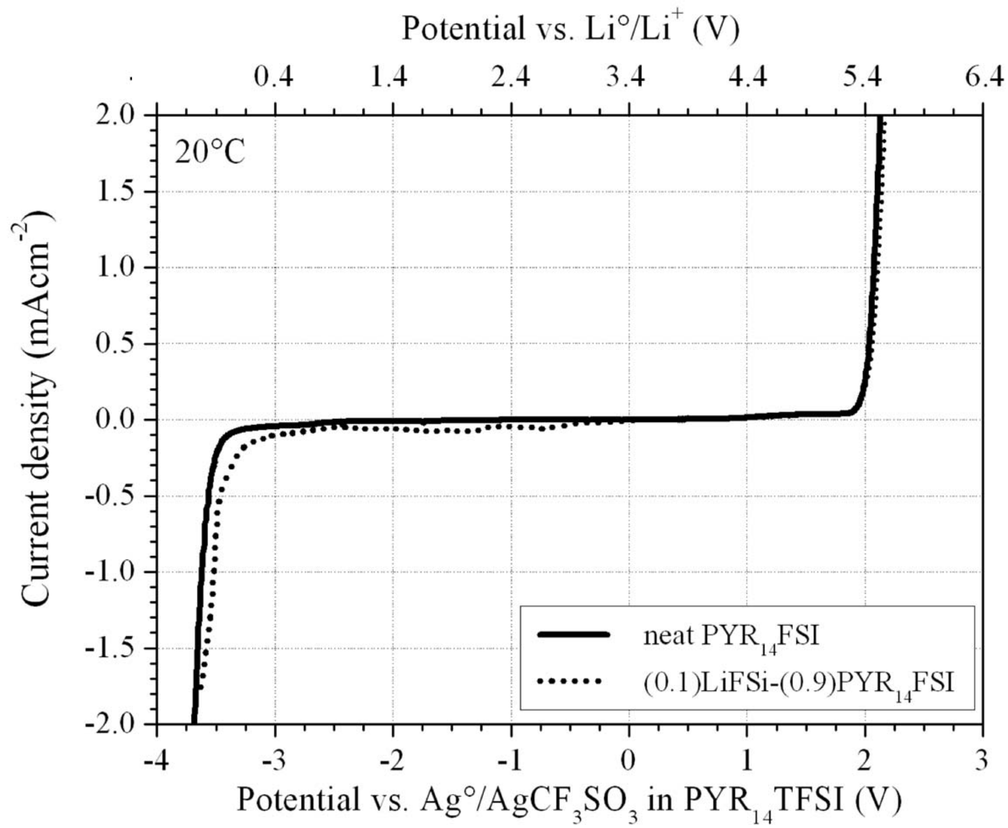
The electrolytic mixtures with x> 0.15 show only glass transition below -60° C

Paillard et al., JES 156, A891(2009) Zhou et al. JPC C 114, 6201 (2010)

LiFSI – $PYR_{14}FSI$ mixtures for electrolytes

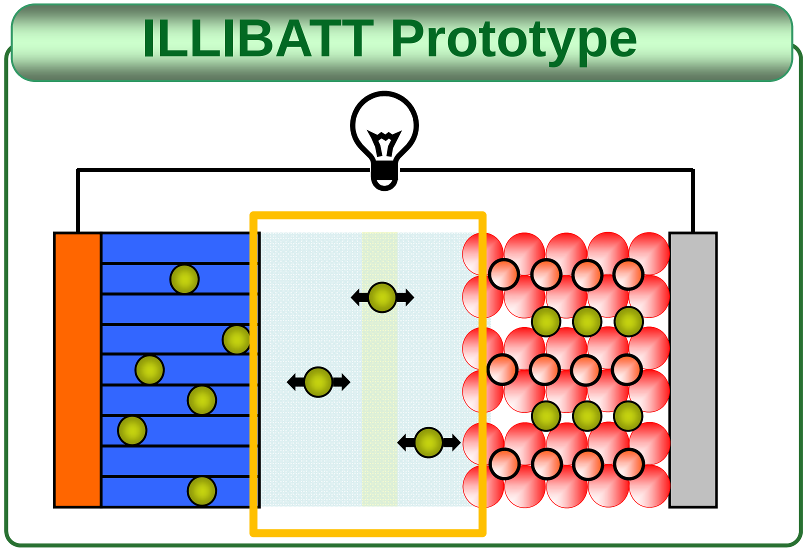


High ionic conductivity at sub-ambient temperatures

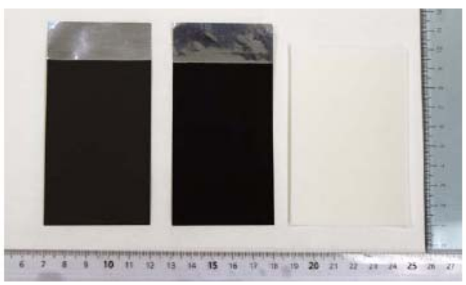


Wide Electrochemical Stability Window (ESW)

Ionic Liquid-based Lithium-ion Batteries



ANODE: $Li_4Ti_5O_{12}$ (LTO)
CATHODE: $LiFePO_4$ (LFP)
BINDER: CMC
ELECTROLYTE: 0.1LiTFSI – 0.9 $PYR_{14}FSI$



ELECTRODES

STACK OF ELECTRODES

ELECTROLYTE

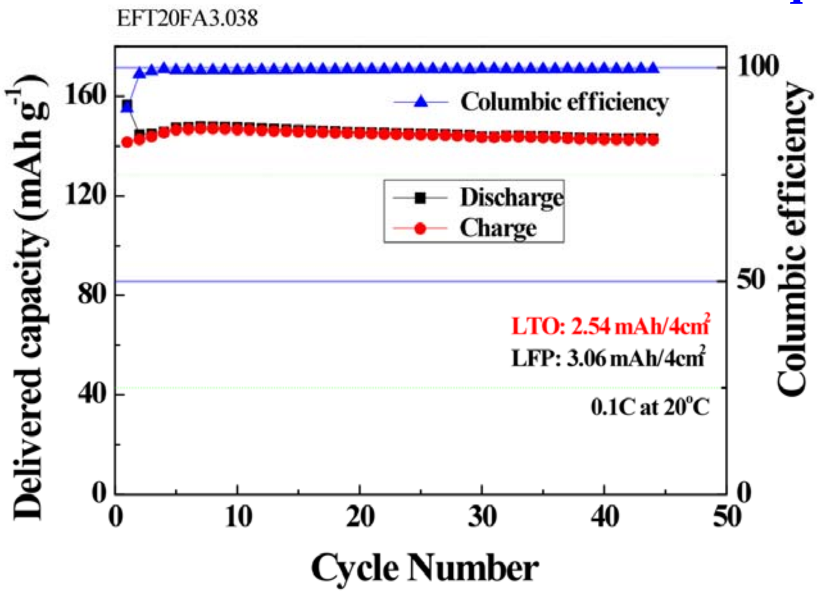
PROTOTYPE

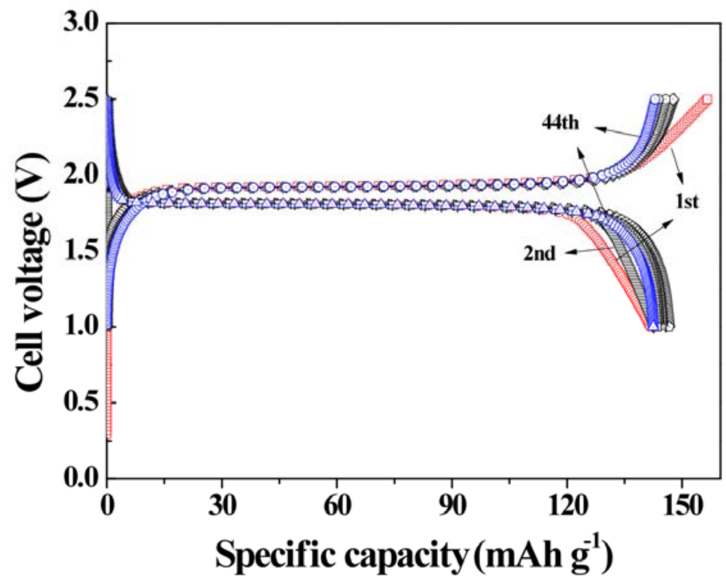
Active material loading: **0.6 – 0.8 mAh/cm²**
Total Capacity: **0.7 – 0.8 Ah**

Stack (12 layers) of bipolar electrodes

Li-Ion cells (LFP-LTO) with Ionic Liquid-based Electrolytes

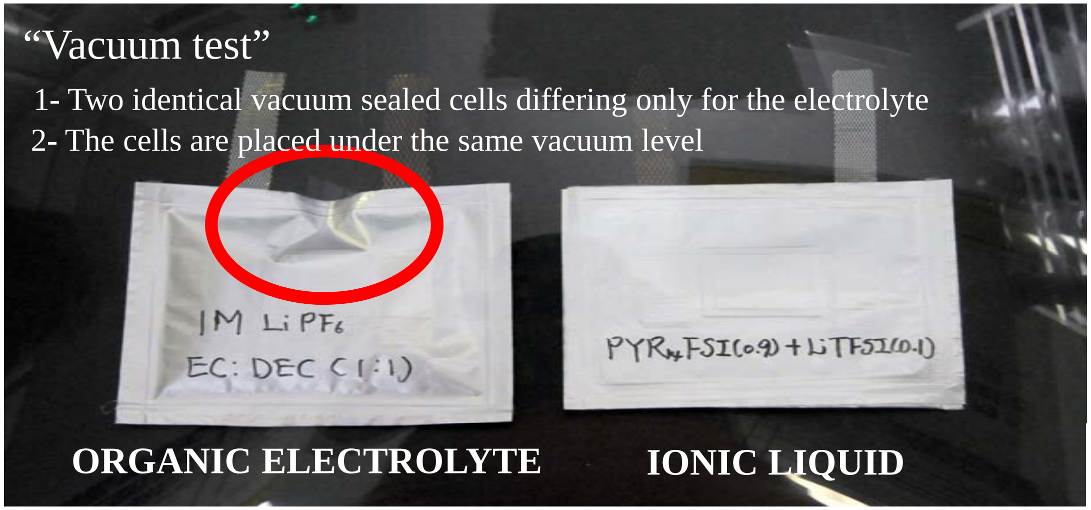
LTO / 0.9PYR$_{14}$FSI – 0.1LiTFSI / LFP
Pouch Cell, glass fiber, 20° C
CMC binder – aqueous slurries – Al collectors





Very promising cycling performance

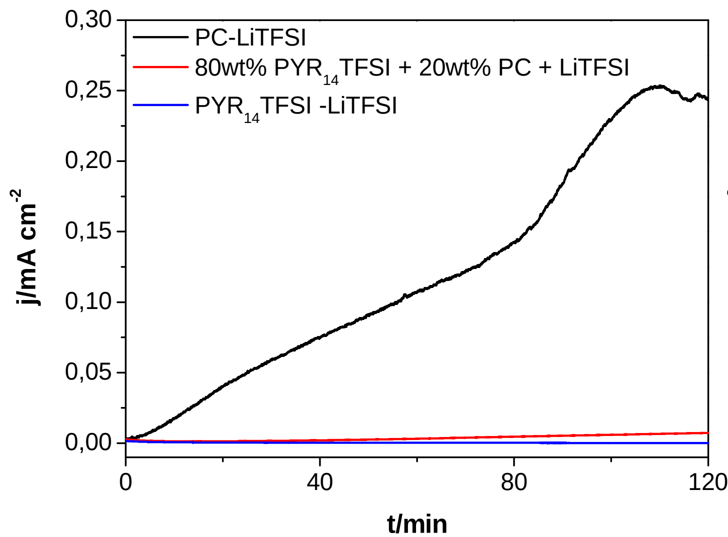
Operation under vacuum

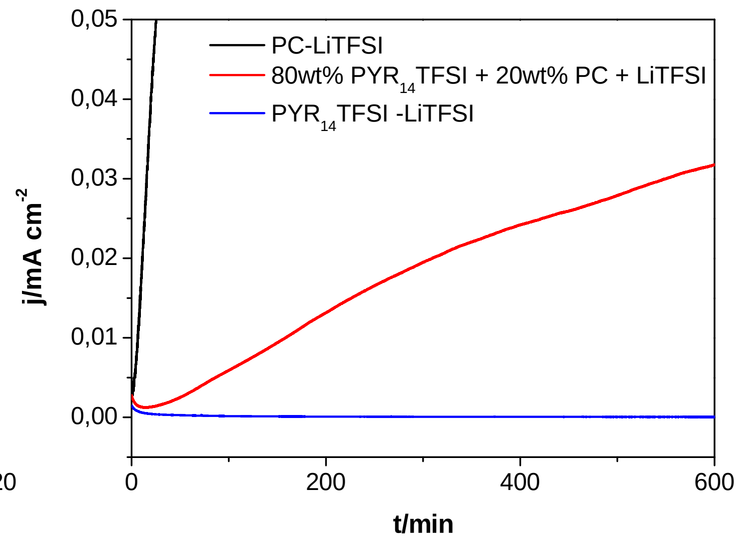


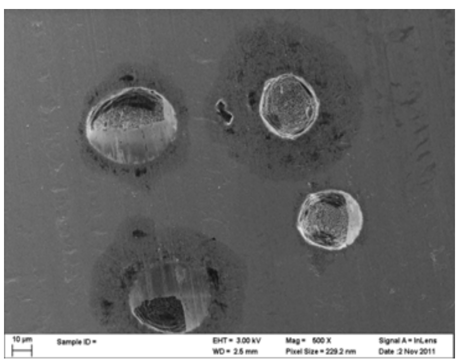
Appetecchi G. B, et al.
J. POWER SOURCES 196, 6703-6709, 2011

Aluminum in PYR_{14}TFSI - LiTFSI electrolytes

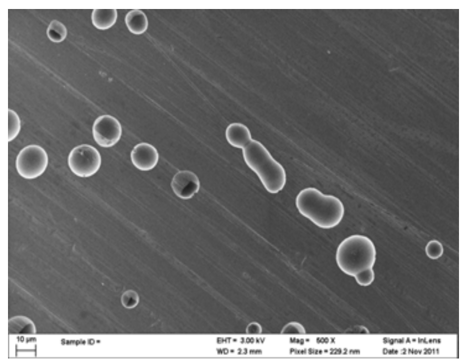
Chronopotentiometry at 4.6 V vs. Li/Li



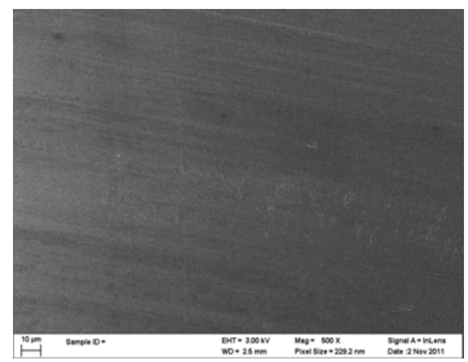




PC-LiTFSI



(80%PYR_{14}TFSI-20%PC)-LiTFSI

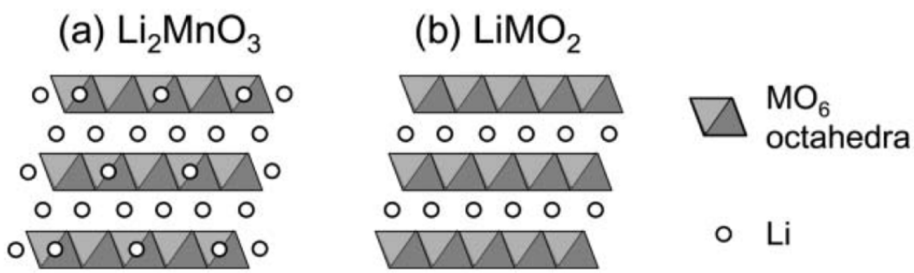


PYR_{14}TFSI-LiTFSI

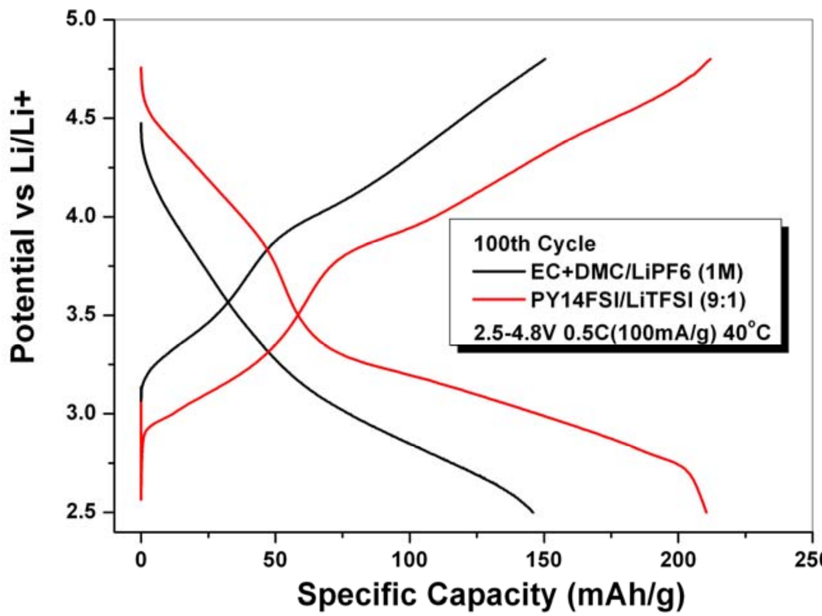
Al corrosion suppressed with TFSI-based electrolytes

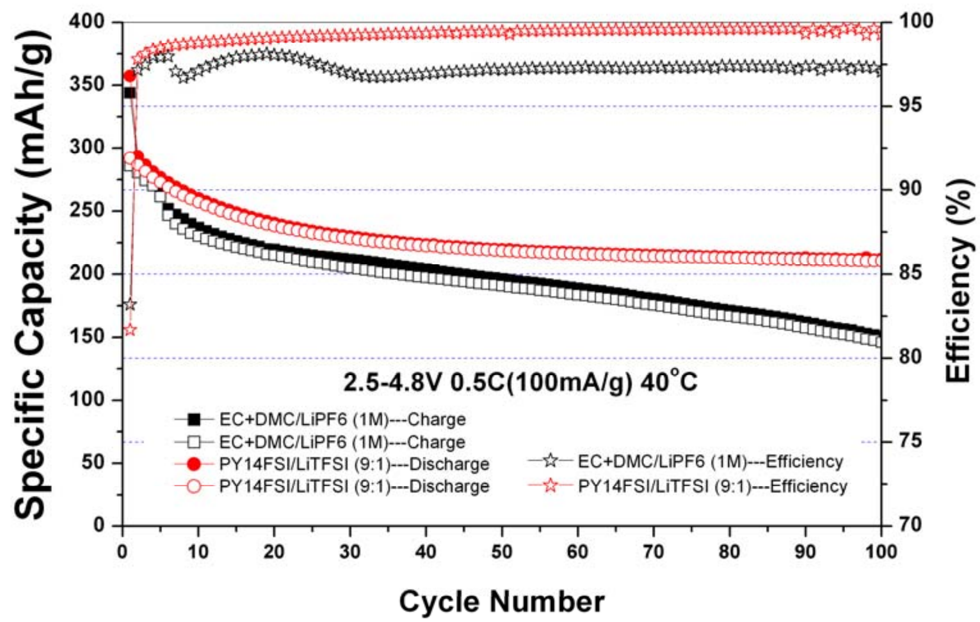
[1] R.-S. Kühnel,et al, J. Power Sources, in press (2012)

High Voltage Electrodes: IL vs Carbonates @ 4.8 V



Li / Electrolyte / $Li[Li_{0.2}Mn_{0.56}Ni_{0.16}Co_{0.08}]O_2$
Pouch Cell @ 40° C and C/2

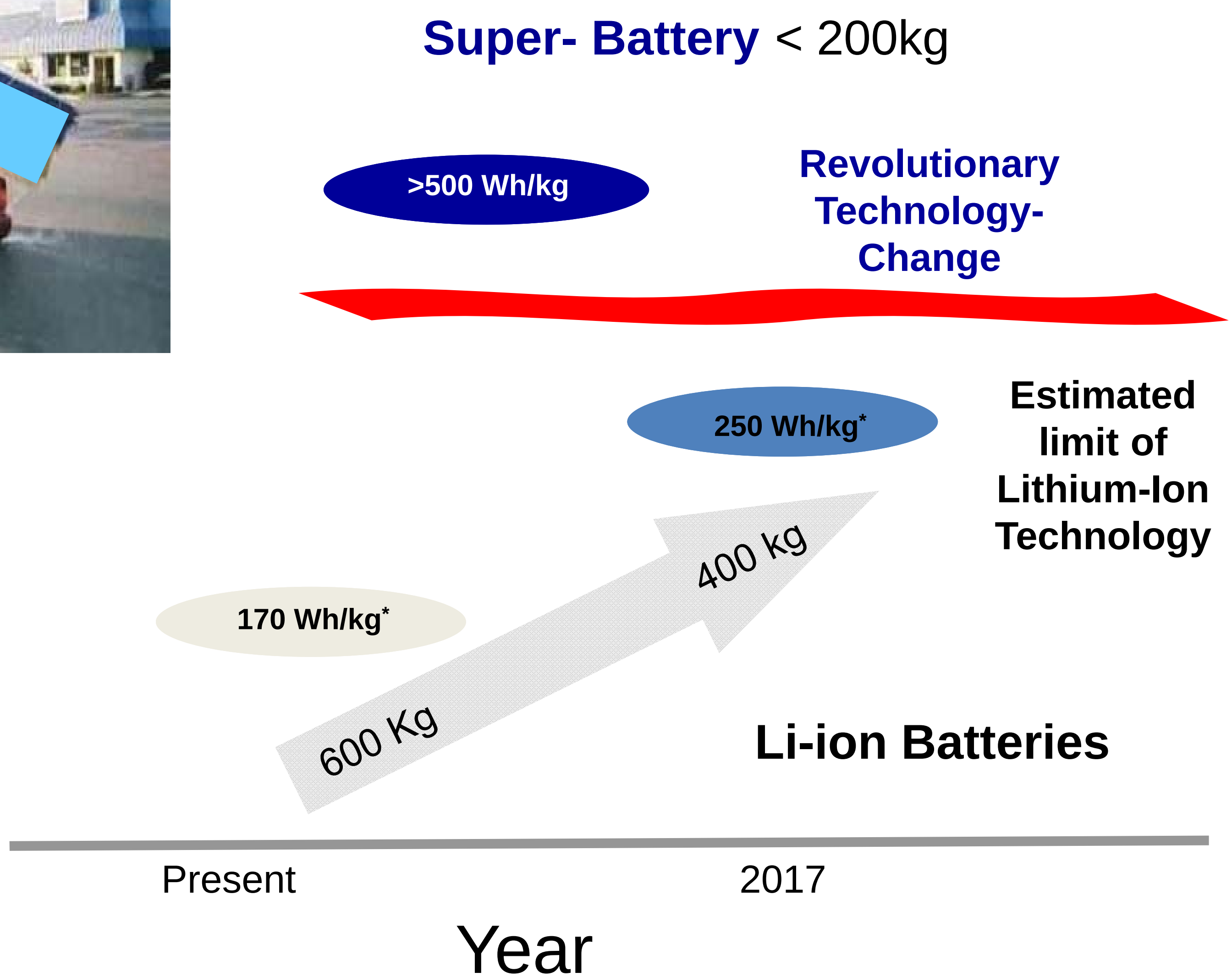




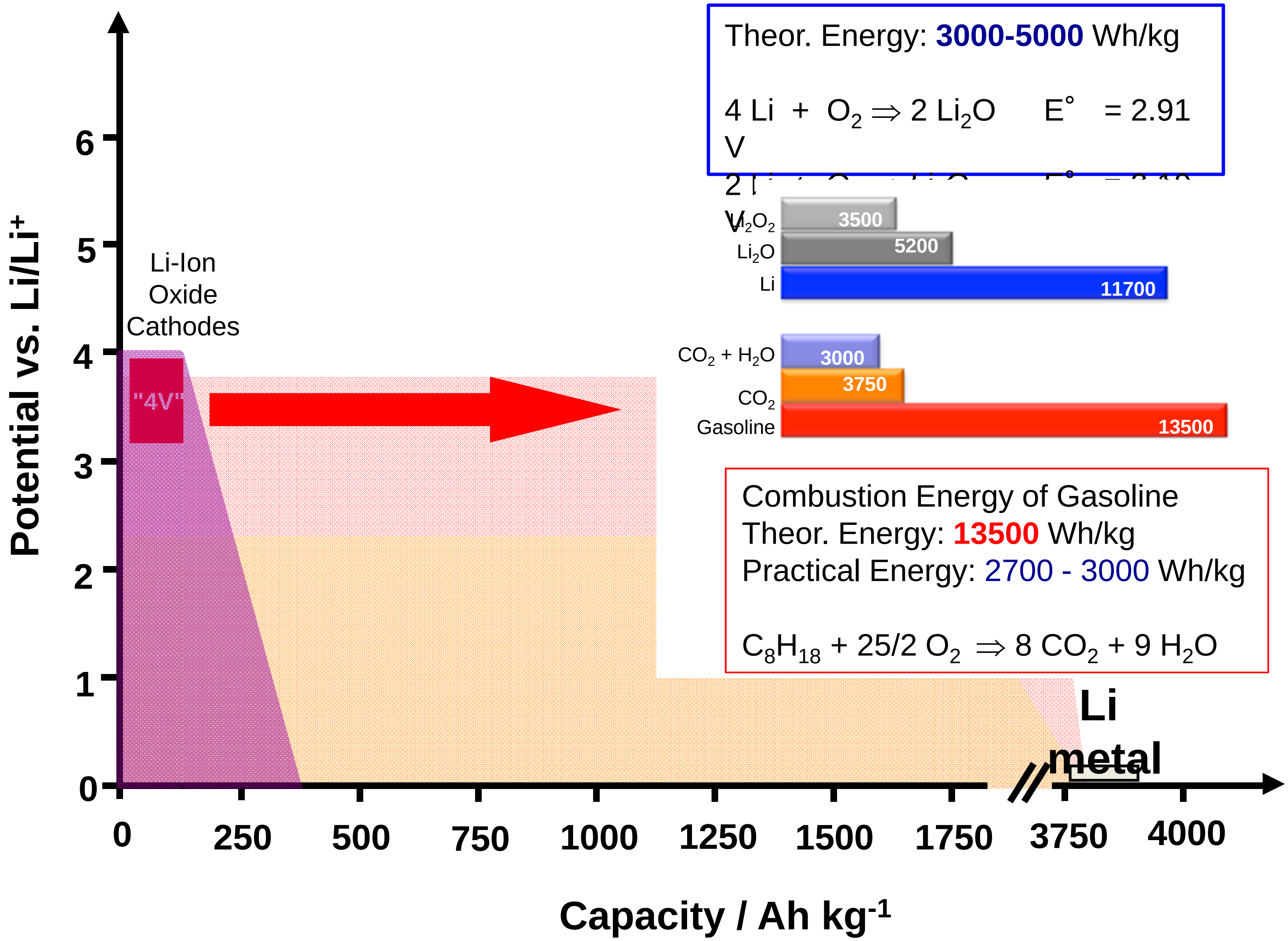
Very high capacity after long-term cycling
High coulombic efficiency (pract. 100%)

High-Energy (Next-Generation) Battery Technologies

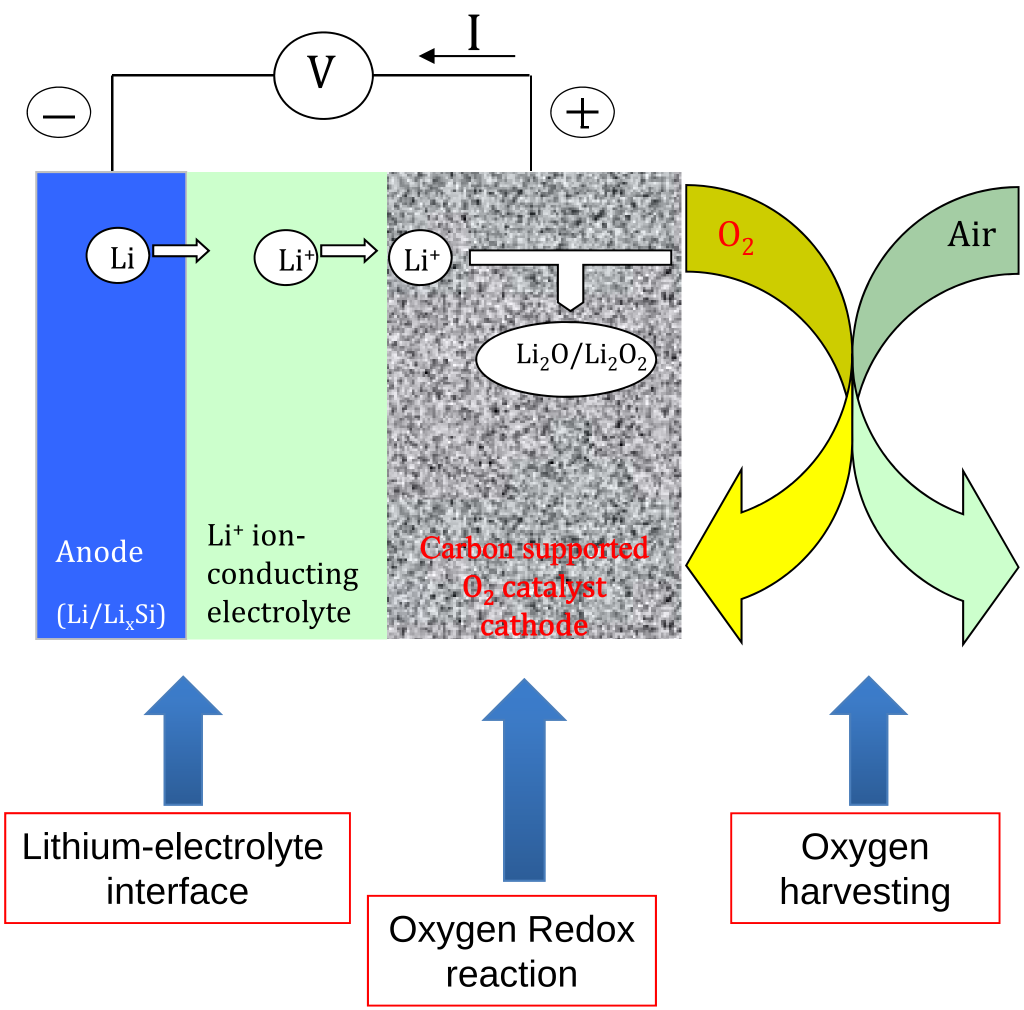
Pb-acid 3000 kg
Ni-MH 1200 kg



Li-Element batteries



Li-Air batteries: Splitting the Issues



KEY ISSUES OPEN

EU Project LABOHR

FP7-2010-GC-ELECTROCHEMICAL STORAGE
265971

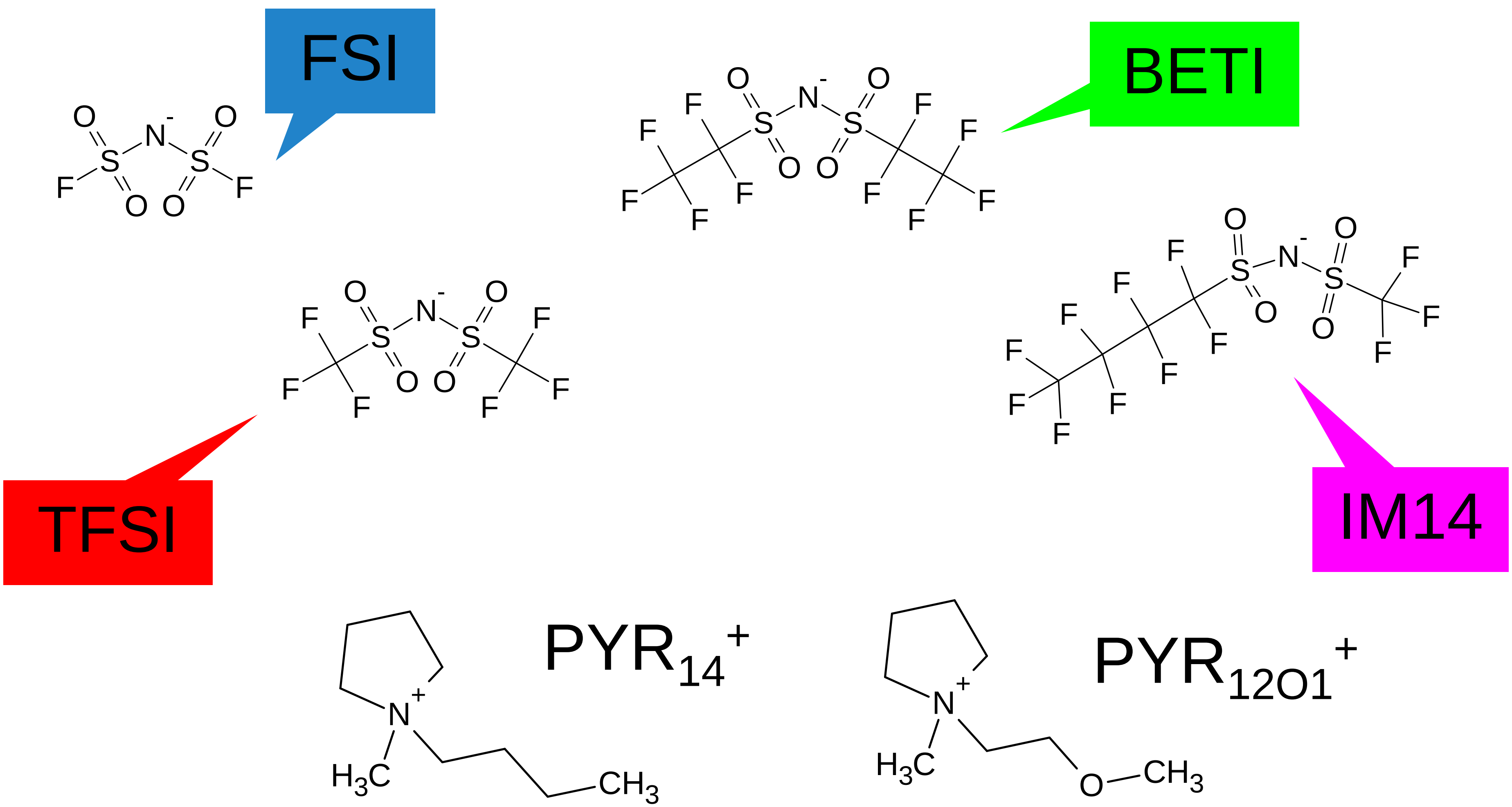
Target:
500Wh/Kg & 200W/kg at the battery pack

Participant organisation name	Country
Westfaelische Wilhelms-Universitaet Muenster (WWU)	DE
Tel Aviv University (TAU)	IL
Consejo Superior de Investigaciones Cientificas (CSIC)	ES
Kiev National University of Technology and Design (KNUTD)	UKR
University of Bologna (UNIBO)	IT
University of Southampton (SOTON)	UK
SAES Getters S.p.A. (SAES)	IT
Chemetall	DE
AVL List GmbH (AVL)	AT
Volkswagen (VW)	DE
European Research Services GmbH (ERS)	DE

Conventional electrolytes based on carbonates and ethers have been ruled out because of insufficient stability for ORR

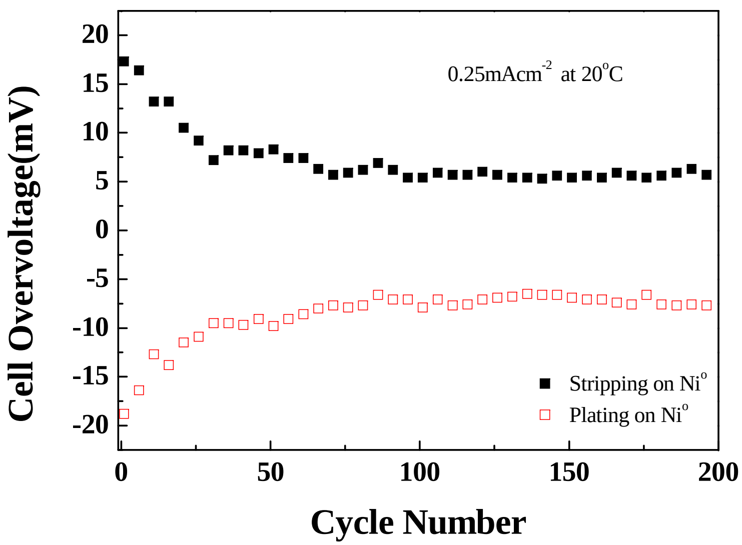
Investigated ILs for Li-Air cells

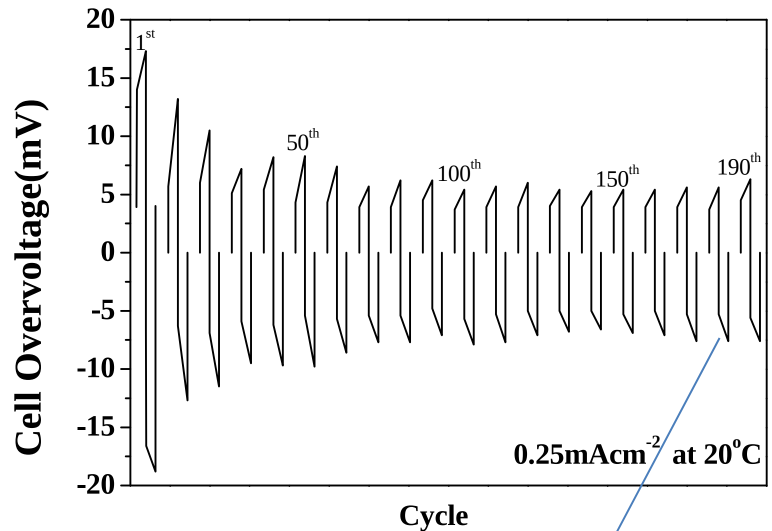
4 anions vs. 2 cations

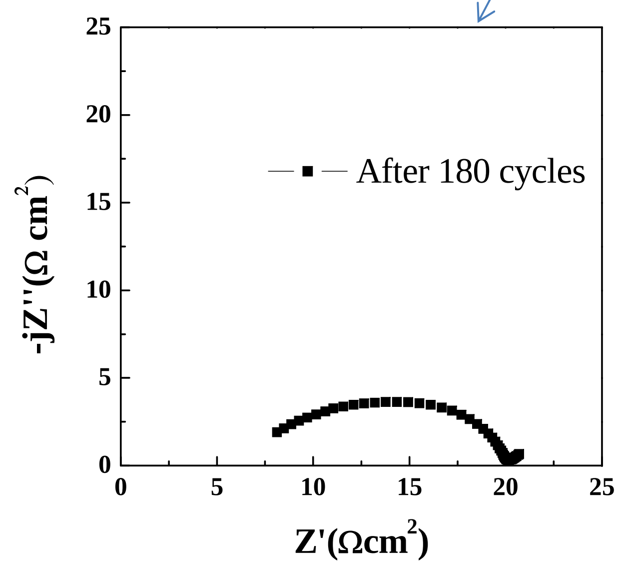


Li plating/stripping from IL-based electrolytes

Li / 0.1LiTFSI-0.9PYR_{14}FSI/Ni (20° C, 0.25 $mAcm^{-2}$, sealed cell)



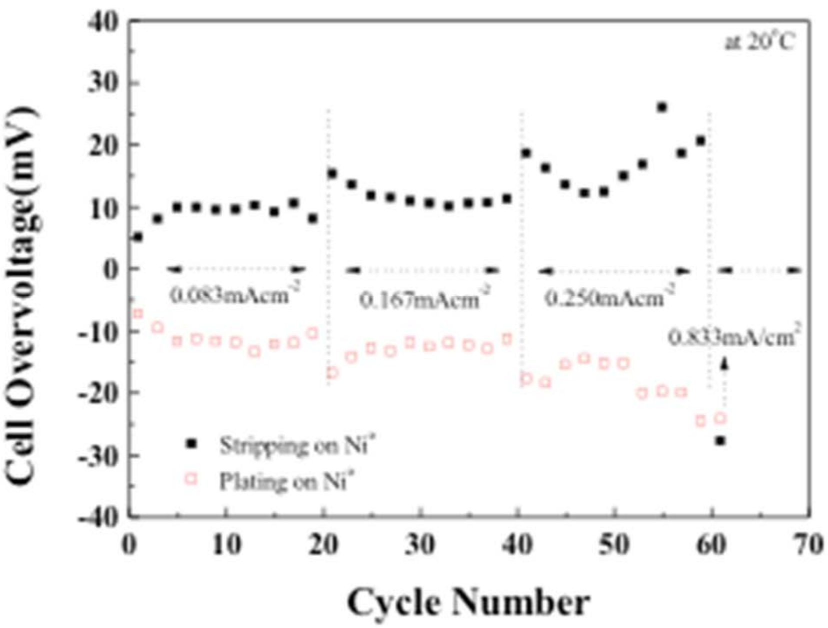


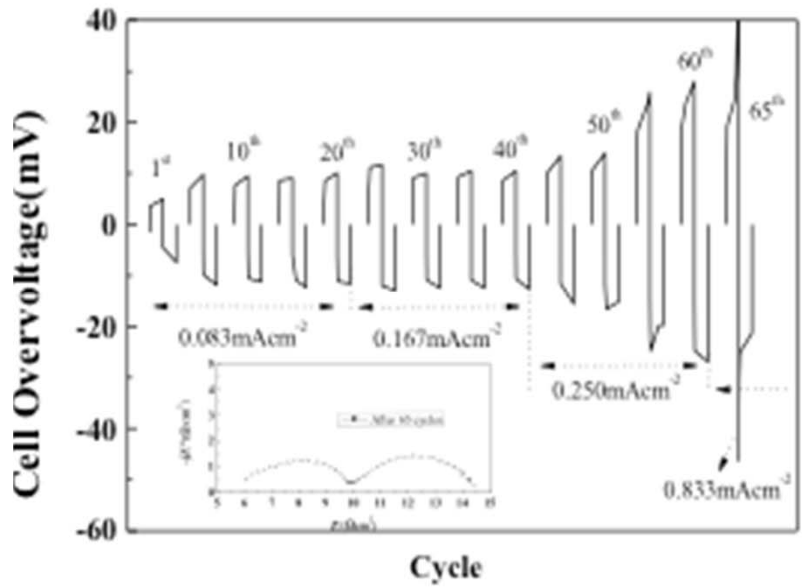


Very promising cycle performance

Li plating/stripping from IL-based electrolytes

Li / 0.1LiTFSI-0.9PYR_{14}FSI/Ni (20° C, various current rates,sealed cell)

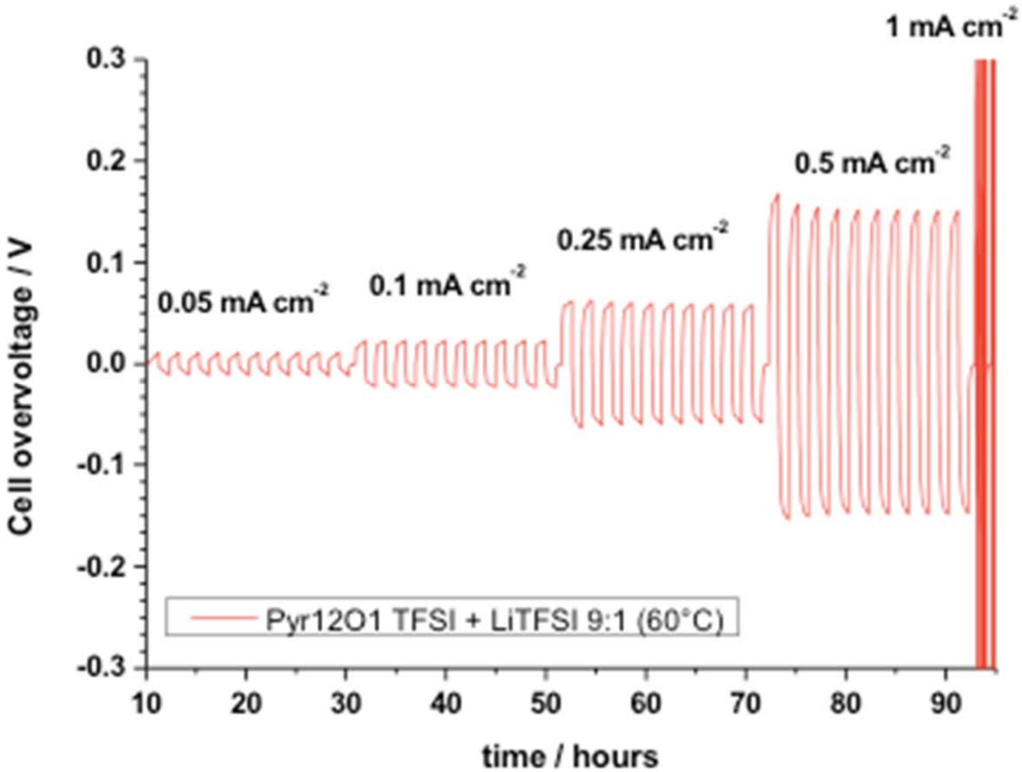




Limited rate performance

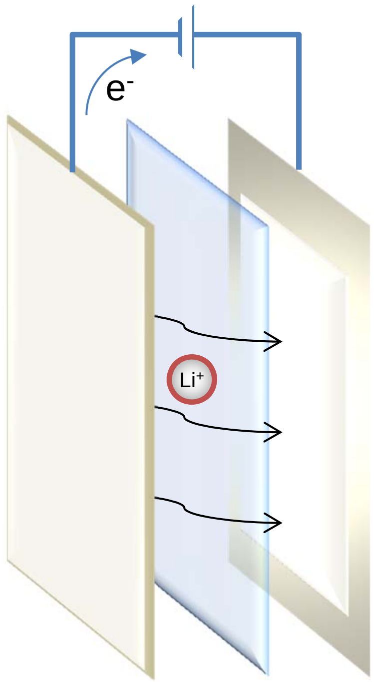
Li plating/stripping from IL-based electrolytes

Li / 0.1LiTFSI-0.9PYR$_{12O1}$TFSI/Li (60° C sealed cell)

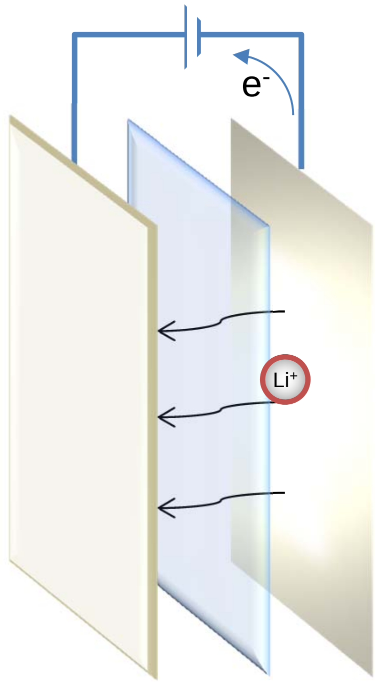


Open challenge: 1 mAcm^{-2}

Effect of (dry) air on Lithium plating/stripping



Li / IL / Ni

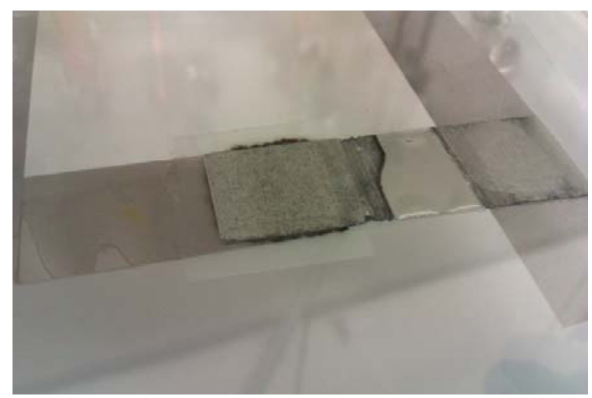


Li / IL / Ni

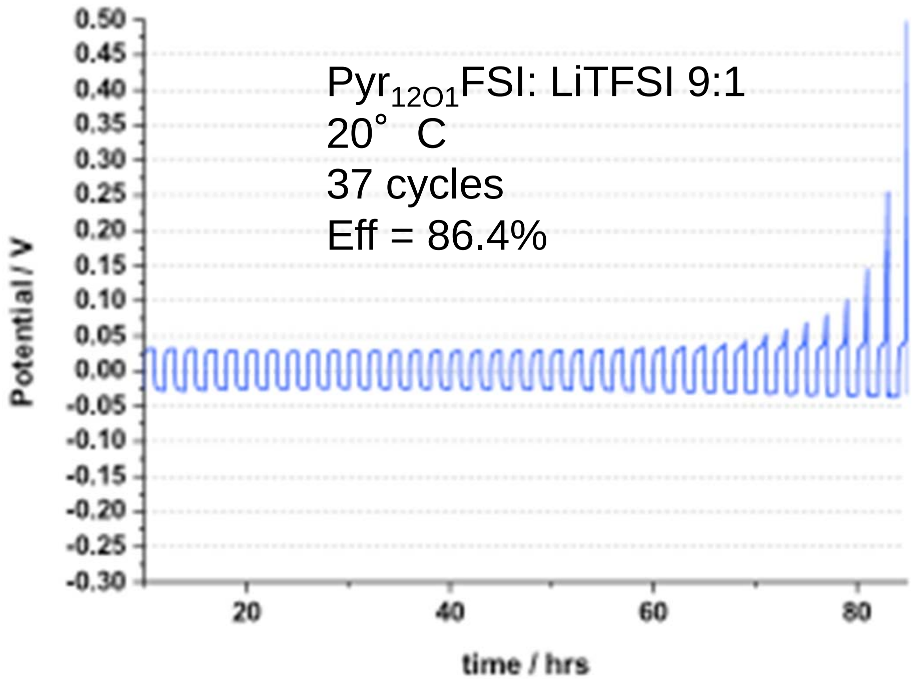
10h plating at 0.1 mA cm^{-2}

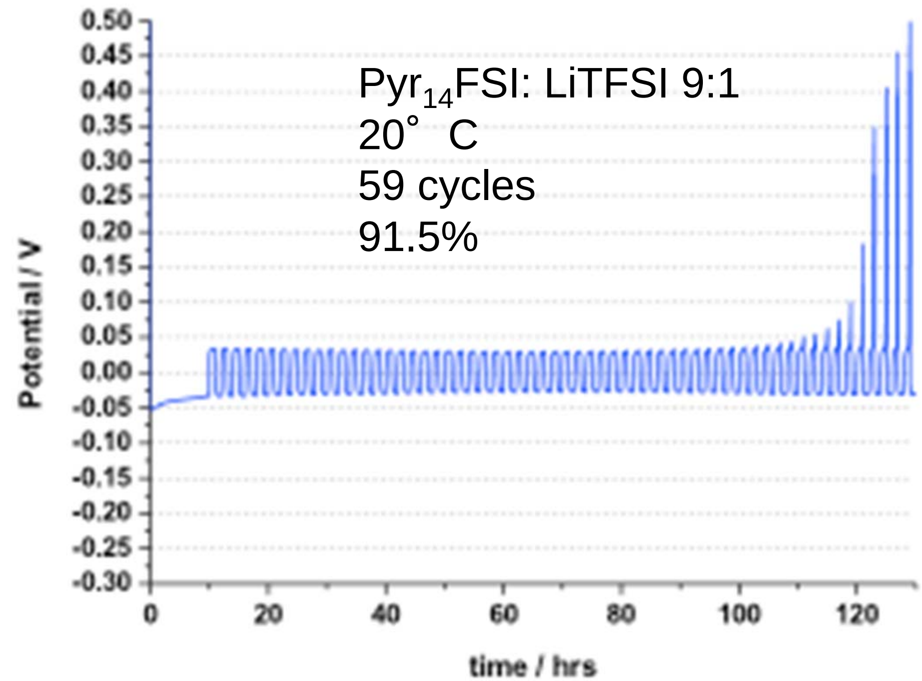
Cycles of 1h stripping / 1h plating
0.1 mA cm^{-2}, $V_{cut\text{-}off}$ = 0.5V

$$Eff = 1 - \frac{Q_p}{2nQ_c}$$



Pyr_{12O1} FSI: LiTFSI 9:1 (open dry air)

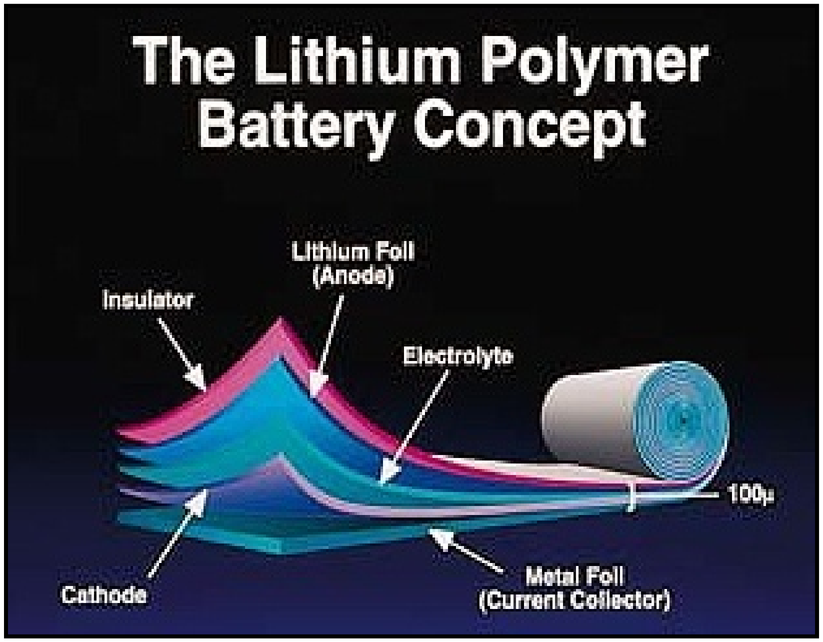




Good cycling performance even in presence of air

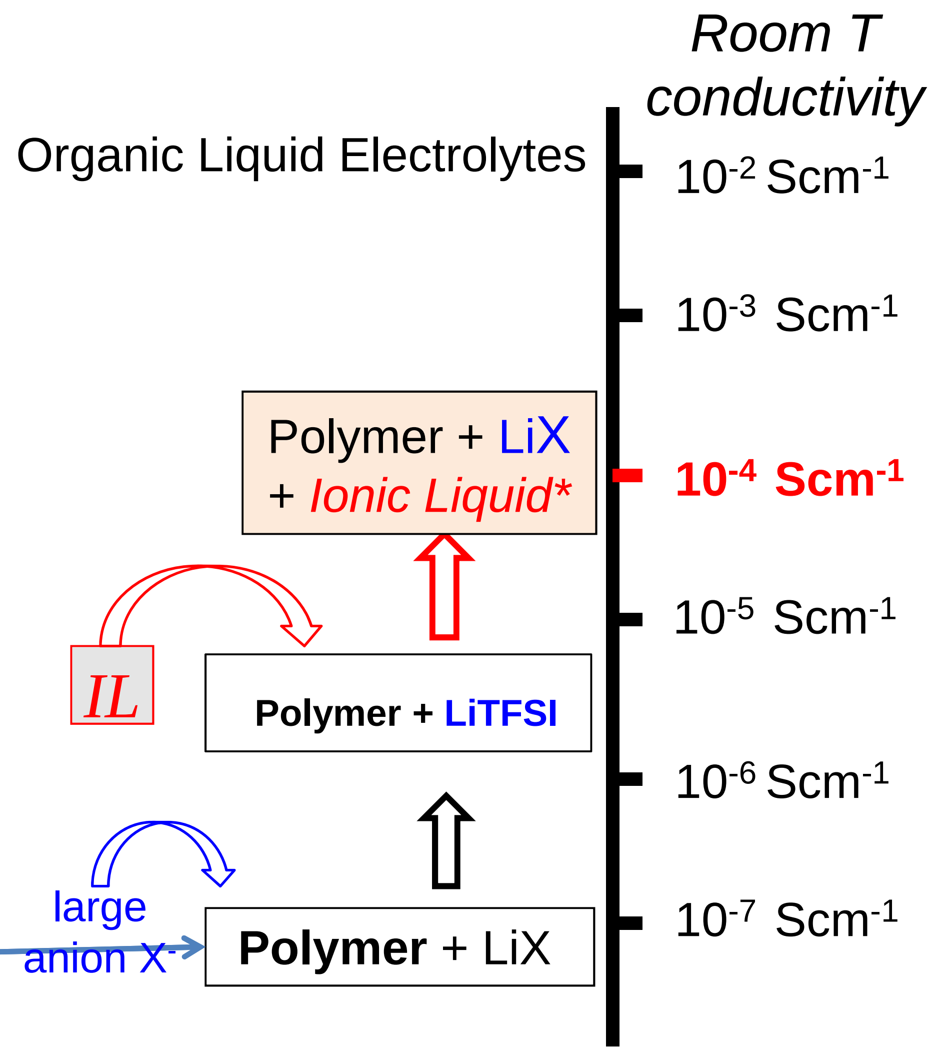
PYR_{14} is more stable than PYR_{12O1} in dry air

Lithium Metal Polymer Batteries (LMPBs)



- **no liquid compounds**
- **high safety**
- **high energy density**
- **very good processability …**

but …. *poor RT conductivity*

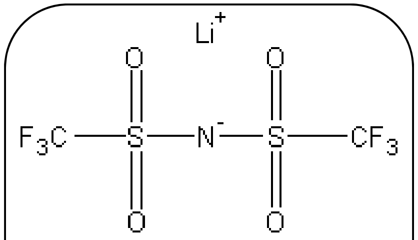


Incorporation of ILs has resulted in high ionic conductivity SPEs

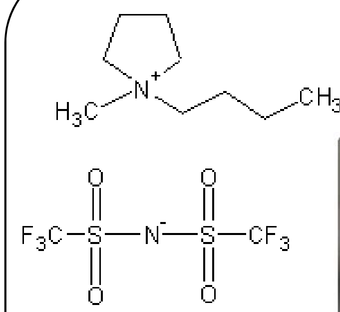
J.-H. Shin, et al.. *Electrochem. Comm.* **2003**, *5*, 1016. Ionic liquids to the rescue? Overcoming the ionic conductivity limitations of polymer electrolytes.

PEO-LiX-IL electrolytes: SPEs

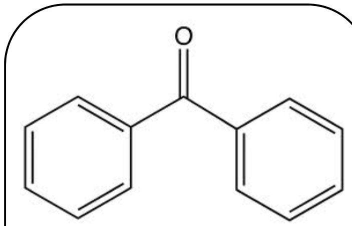
Poly(ethylene oxide)
PEO, n ~ 91.000
Molecular weight ~ 4 Mio.



Li TFSI

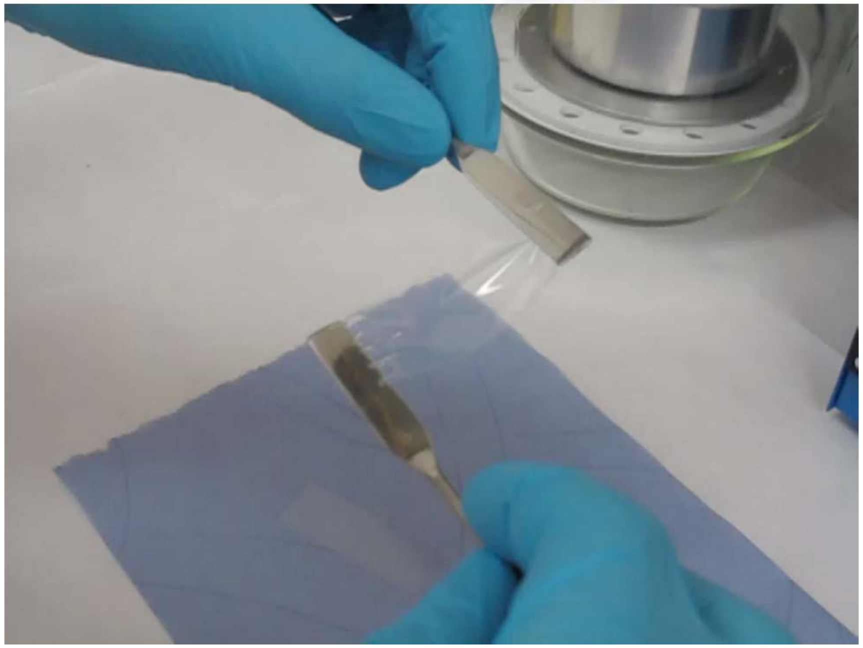


$PYR_{14}TFSI$



Benzophenone

<u>Composition is given as</u>:
Molar ratio of P(EO) : Li salt : IL
[20 : 2 : 4]

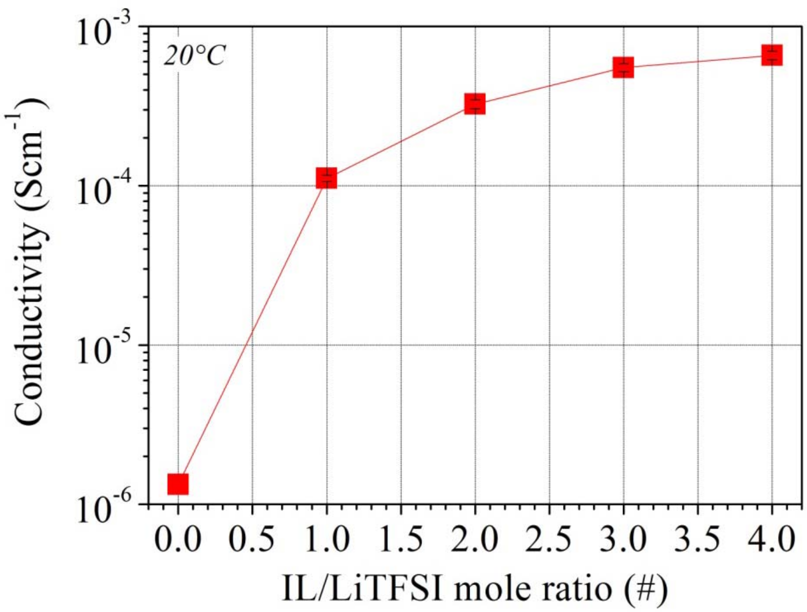


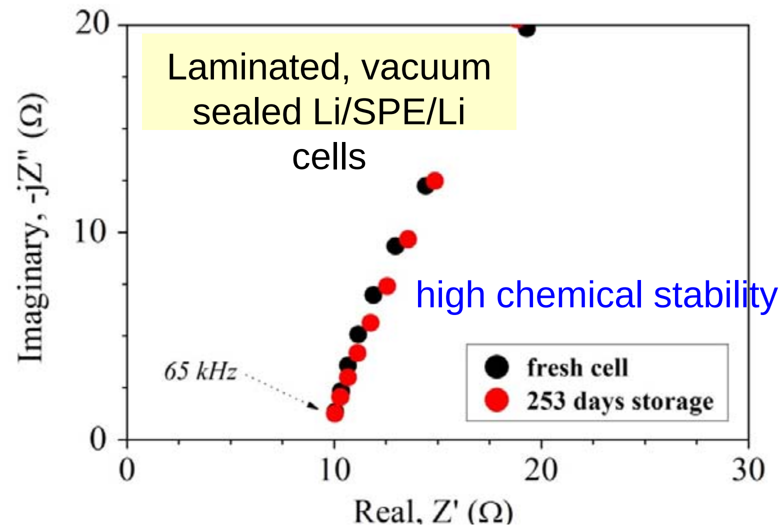
Good adhesiveness

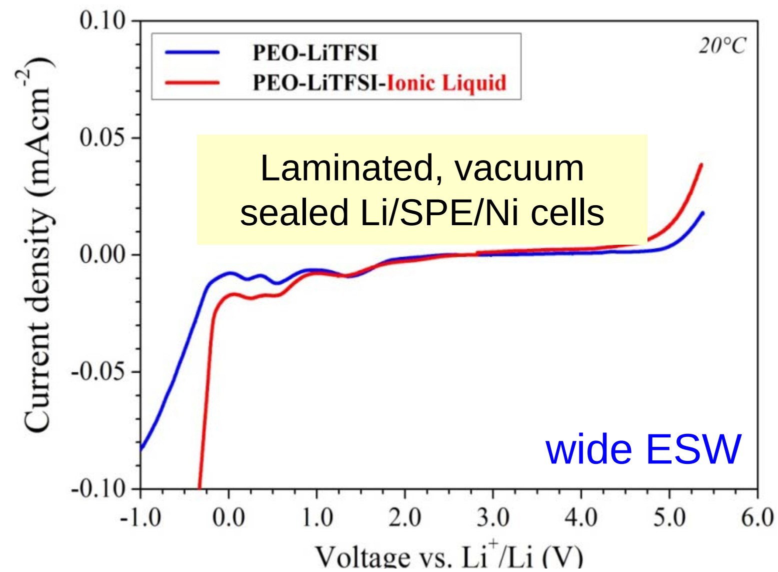
Excellent mechanical properties

PEO-LiX-IL electrolytes: conductivity and stability

PEO : LiTFSI : $PYR_{14}TFSI$ = 20:2:4 (mol)



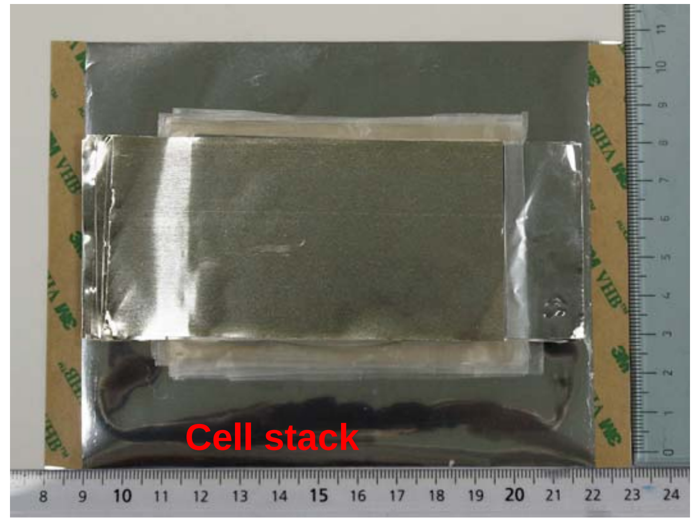




High ionic conductivity

Excellent mechanical, chemical and electrochemical stabilities

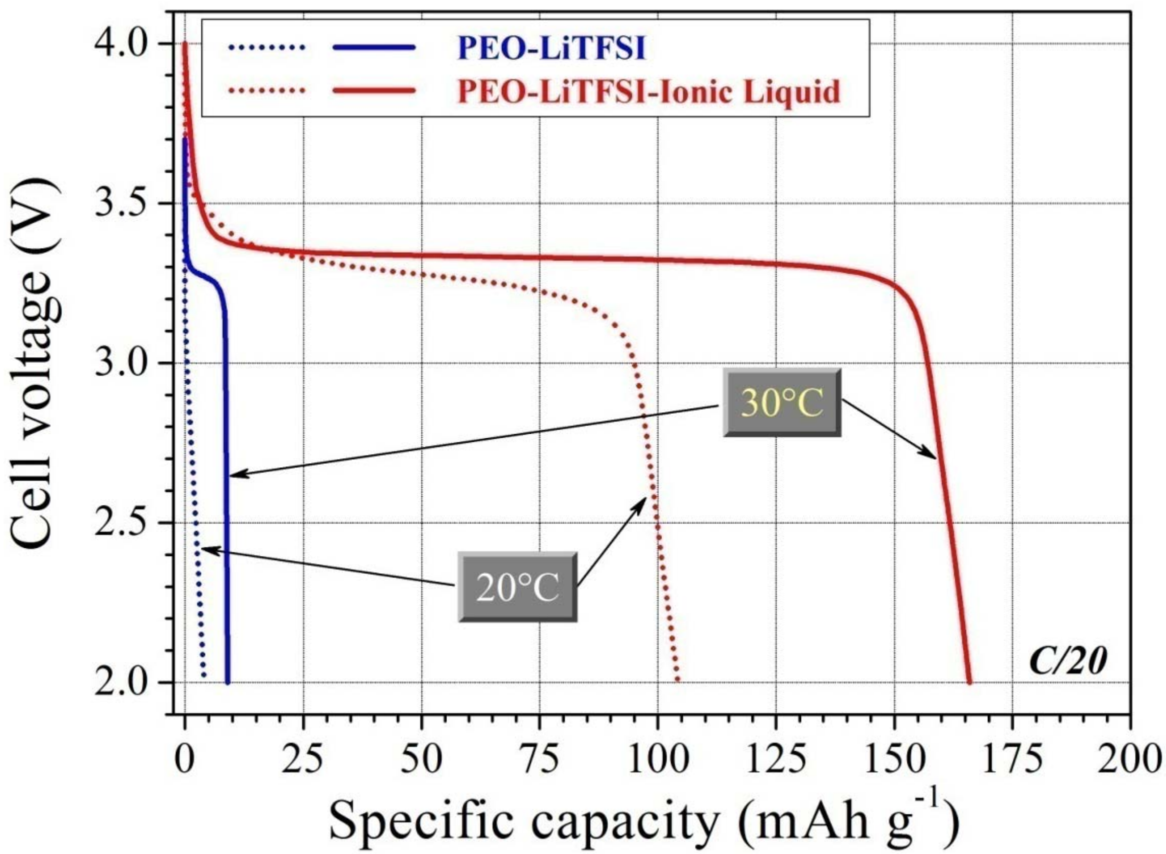
Lithium metal electrode operation appears feasible in IL-based electrolyte



Li/ IL-based electrolyte/ LFP
1Ah prototype

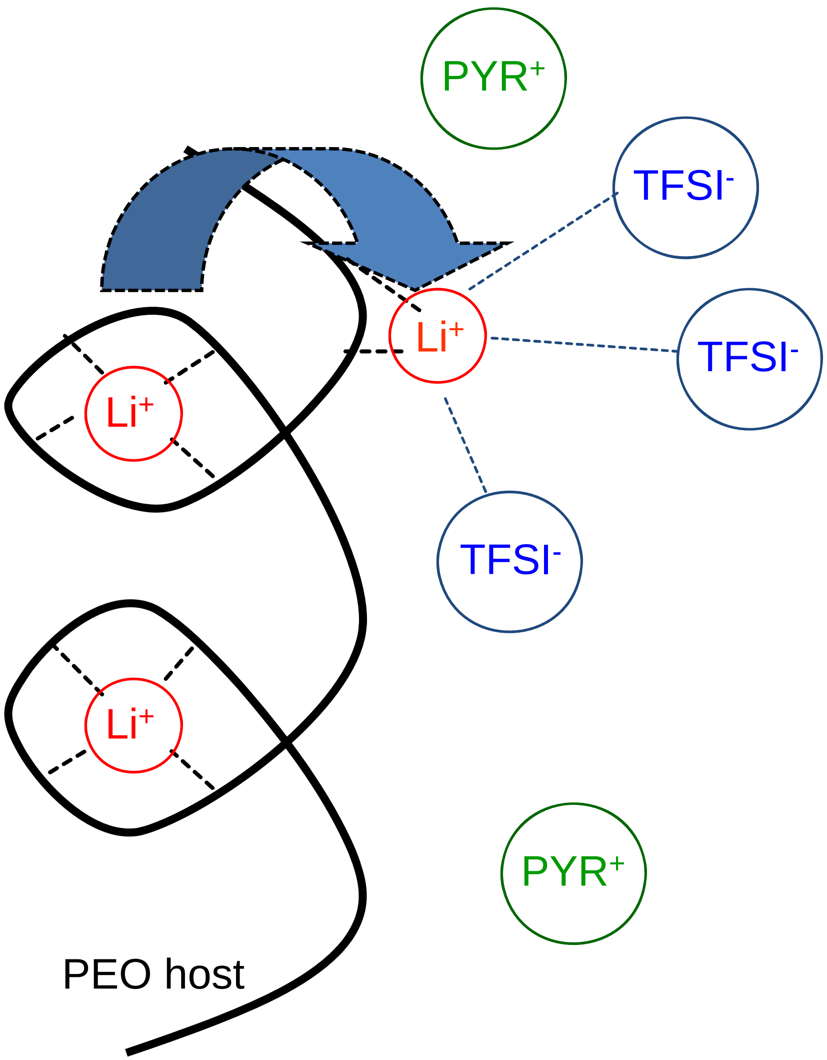
Battery tests: PEO-IL-LiX electrolyte (RT tests)

Li / $P(EO)_{10}LiTFSI\text{-}PYR_{14}TFSI$ / $LiFePO_4$



- Very large capacity increase due to IL incorporation > 100 mAhg^{-1} at 20°C
- Theoretical capacity (170 mAhg^{-1}) at 30°C

PEO-LiX-IL electrolytes
How do ILs enhance Li^+ conduction?



PEO-LiX electrolyte: Li^+ is strongly coordinated by PEO host

PEO-LiX-IL electrolyte:

solid ternary system composed by a polymer host (PEO) and two salts (LiTFSI and PYR_{14}TFSI)

- very weak interactions between PYR_{14}^+ and $TFSI^-$ [1]
- no interaction between PYR_{14}^+ and PEO host (Raman & NMR) [2,3]
- **strong interactions between Li^+ and $TFSI^-$ (in excess)**

the strength of the Li--PEO coordination lowered

the lithium mobility (Li^+ conduction) is promoted

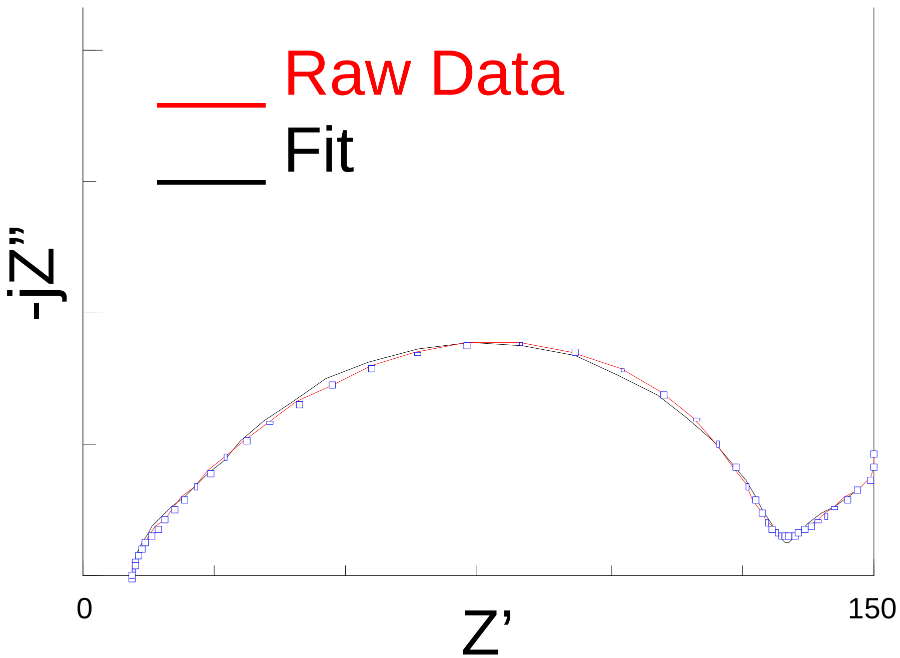
[1] M. Castriota, T. Caruso, R. G. Agostino, E. Cazzanelli, W. A. Henderson, and S. Passerini, *J. Phys. Chem.* A **109** (2005) 92

[2] I. Nicotera, C. Oliviero, W. A. Henderson, G. B. Appetecchi, and S. Passerini *J. Phys. Chem. B* **109** (2005) 22814.

M. Joost et al, Electrochim. Acta, in press 2012

PEO-LiX-IL electrolytes: Li interface (40° C)

Li / $P(EO)_{20}(LiTFSI)_2(PYR_{14}TFSI)_n$ / Li



R_1 = bulk electrolyte resistance

R_2 = Li/SPE interface 1

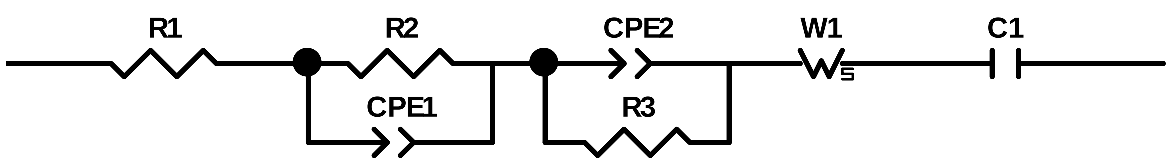
CPE_1 = Li/SPE interface 1

R_3 = Li/SPE interface 2

CPE_2 = Li/SPE interface 2

W_1 = Warburg impedance

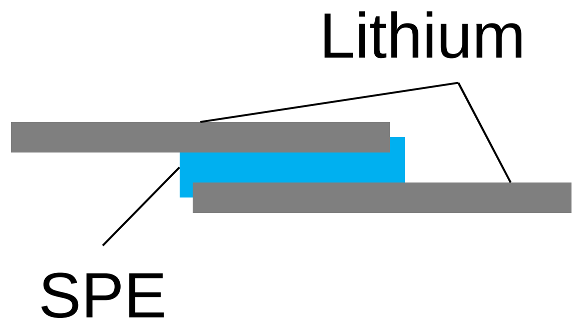
C_1 = electrode limit capacitance



Impedance is localized at the Li/SPE interface

Transport properties by DC tests

How much current can be flown through the SPE?



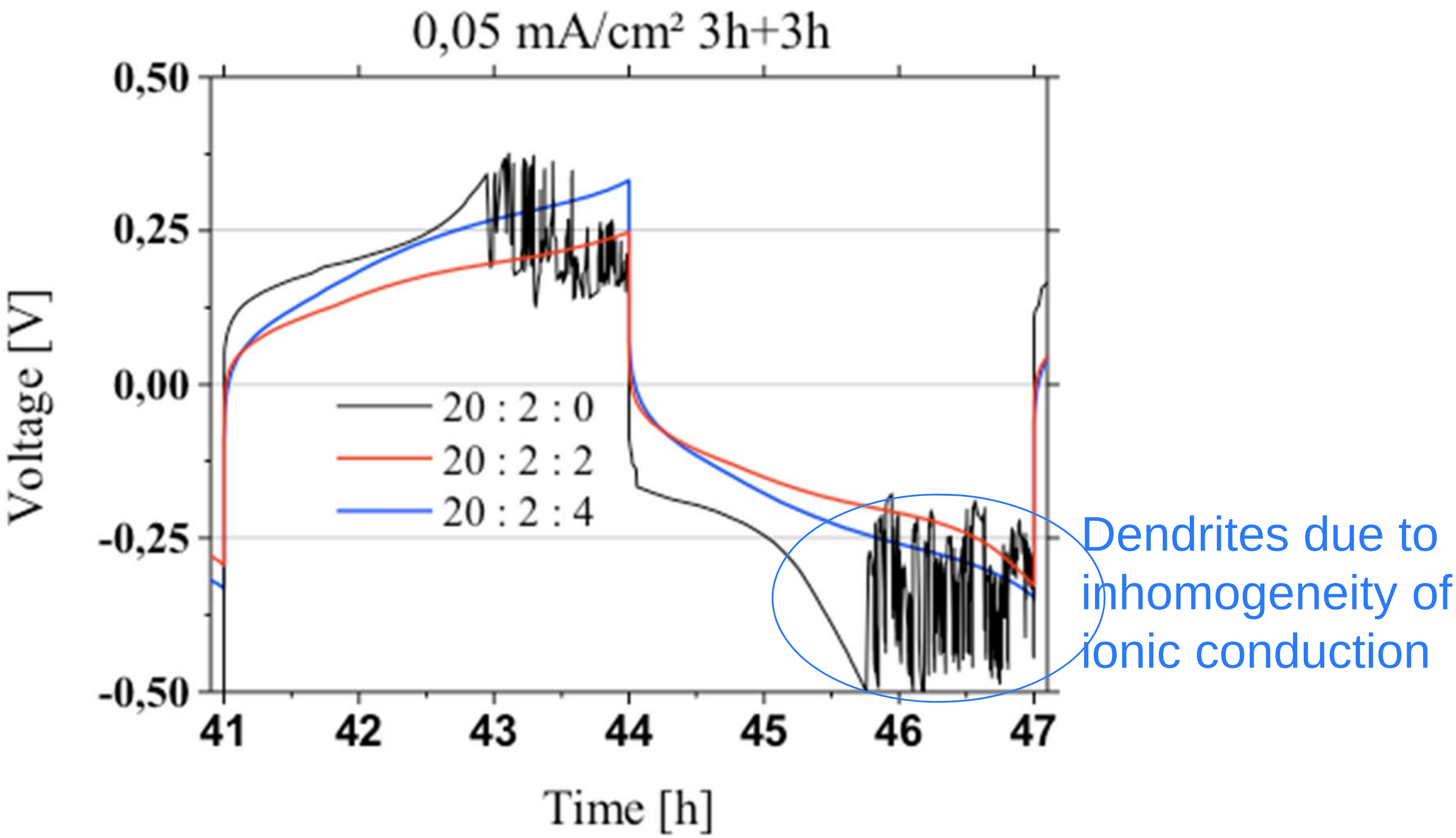
Galvanostatic and Potentiostatic experiments

<u>Capacity of Li foil (Chemetall)</u>:

50 µm * 1 cm² = 5mm³ → **10.32 mAh/cm²**

Transport properties by galvanostatic tests (30° C)

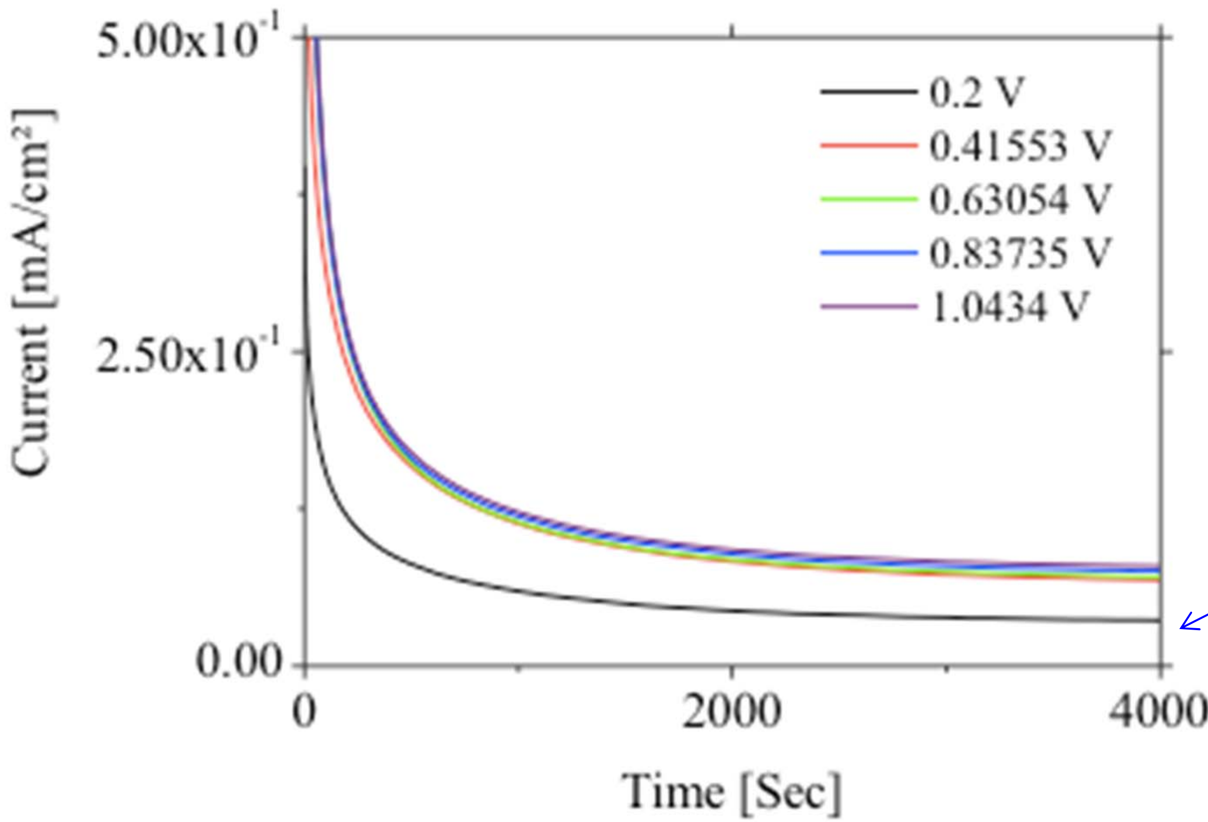
Li / $P(EO)_{20}(LiTFSI)_2(PYR_{14}TFSI)_n$ / Li



IL containing electrolytes perform well at 30° C

Transport properties by potentiostatic tests (30° C)

Li / $P(EO)_{20}(LiTFSI)_2(PYR_{14}TFSI)_4$ / Li

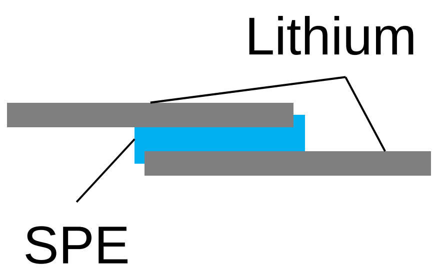


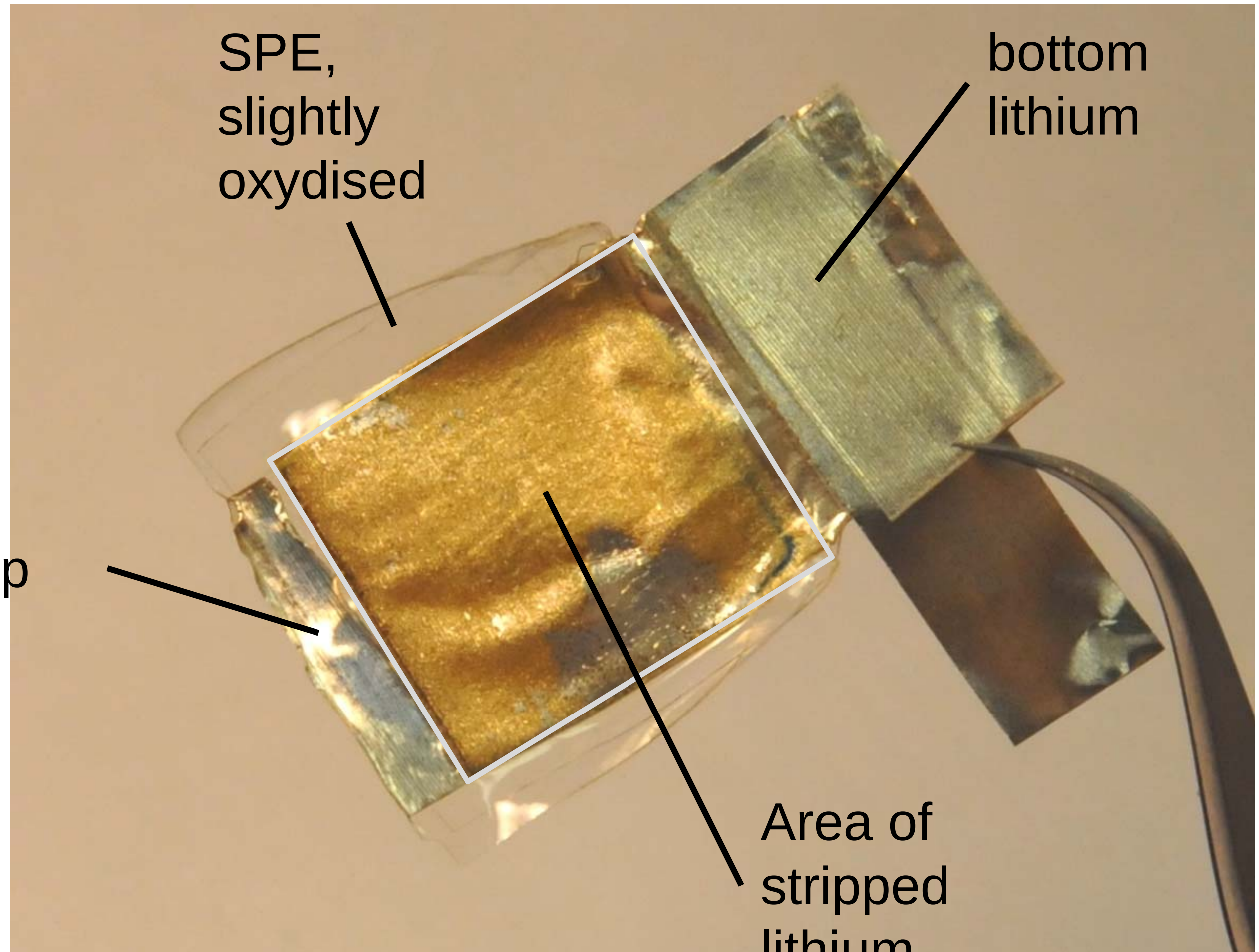
0.05 $mAcm^{-2}$ @ 0.2 V

Good agreement between galvanostatic and potentiostatic results

Transport properties by DC tests

Li / $P(EO)_{20}(LiTFSI)_{2}(PYR_{14}TFSI)_{n}$ / Li



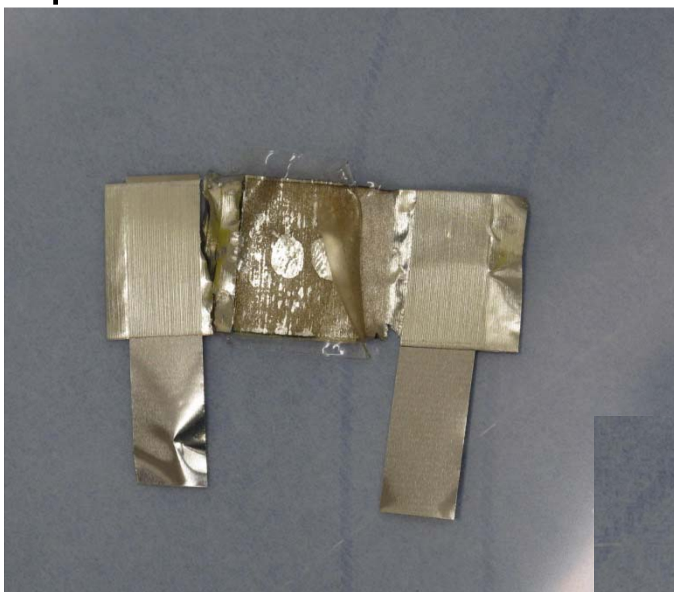


Complete stripping of 50 μm of lithium (ca. 10 mAh cm^{-2})

Transport properties by DC tests

$Li / P(EO)_{20}(LiTFSI)_2(PYR_{14}TFSI)_n / Li$

Open cell



Plated lithium

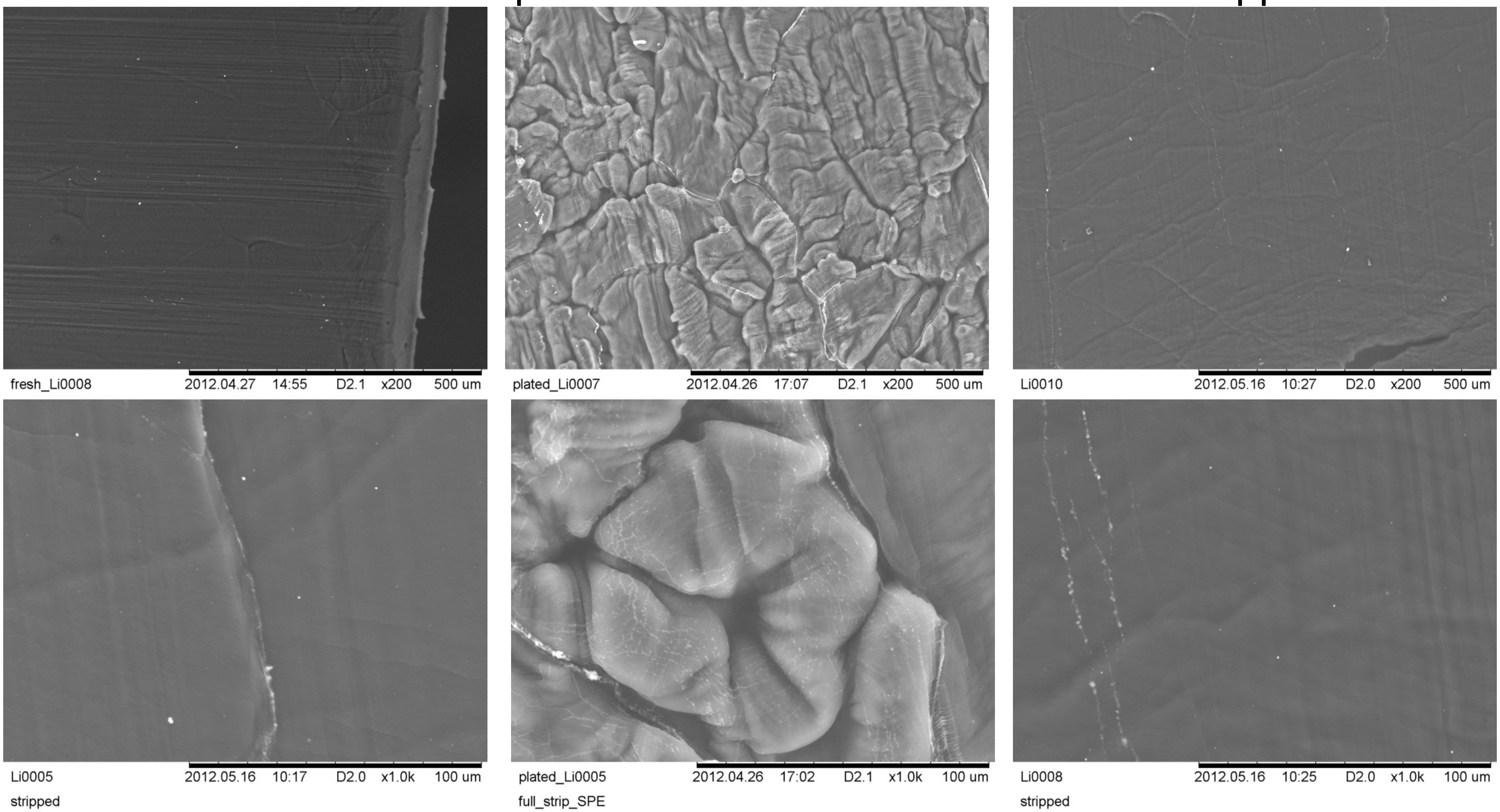
SPE

Opened cell after full lithium plating

Transport properties by DC tests

Li / P(EO)$_{20}$(LiTFSI)$_{2}$(PYR$_{14}$TFSI)$_{n}$ / Li

fresh lithium | plated lithium | SPE on stripped lithium



SEM of fresh lithium, plated lithium and SPE

Conclusions

Ionic Liquid mixtures with lithium salts as such and in presence of polymers show very promising performance as Li-ion conductors.

IL-based electrolytes:

- easy to recycle (low volatility)
- wide storage temperature range
- low flammability components
- high temperature operation capability (>60° C)

IL-based electrolytes appear promising for safe, high energy and moderate power applications (such as full EV and stationary storage).

Acknowledgements

German and NRW funding agencies

The European Commission for the financial support of the projects:

ILLIBATT (**I**onic **L**iquid based **LI**thium **BATT**eries)

LABOHR (**L**ithium – **A**ir **B**atteries with split **O**xygen **H**arvesting and **R**eduction processes)

GREEN LION (Advanced Manufacturing Processes for Low Cost **GREEN**er **L**i-**ION** Batteries)

All members of WWU-MEET and ENEA battery groups

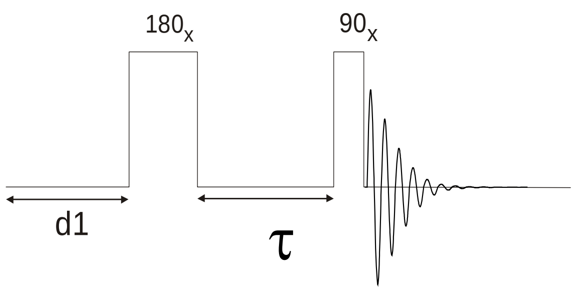
Back up

Methods

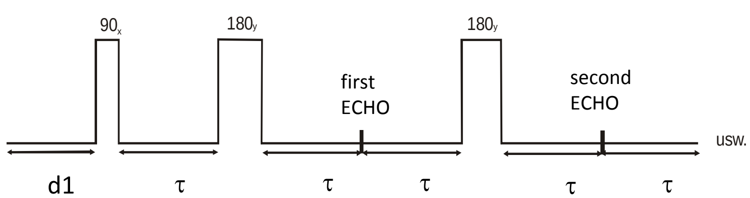
local motion

relaxation measurements

1) spin-lattice-relaxation time T_1: inversion recovery



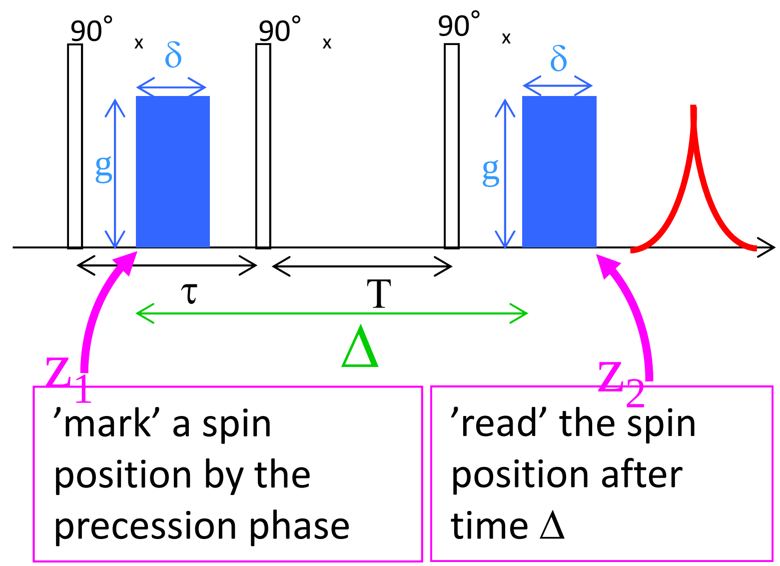
2) spin-spin-relaxation time T_2: CPMG-sequence



macroscopic motion

diffusion measurements:

pulsed gradient stimulated echo sequence



g: gradient strength

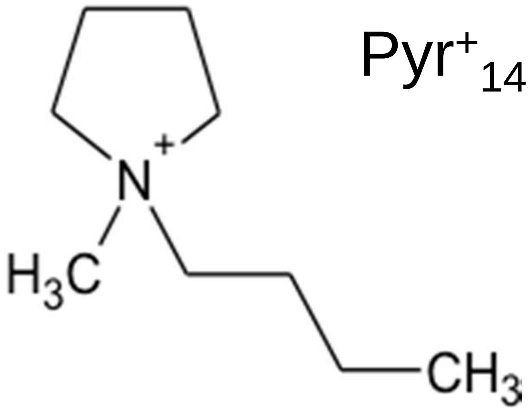
δ: gradient duration

Δ: diffusion time

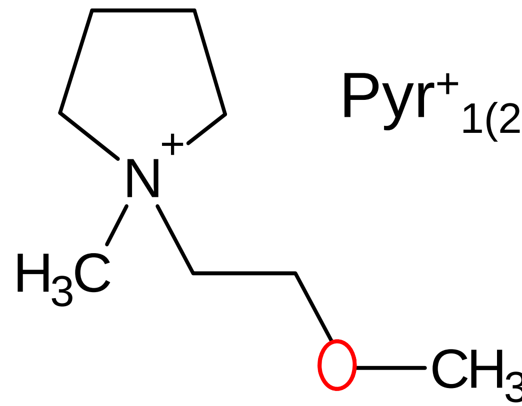
τ: evolution time

z_1 and z_2: spin position before and after the gradients

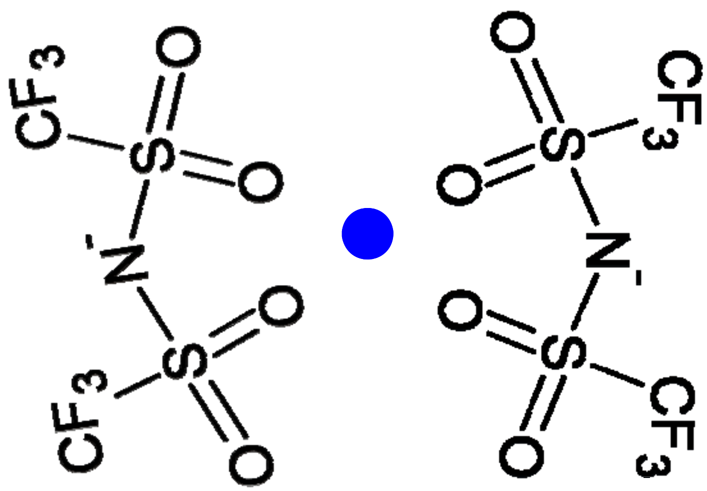
Is the Li^+ --- $TFSI^-$ ion-pairing avoidable?

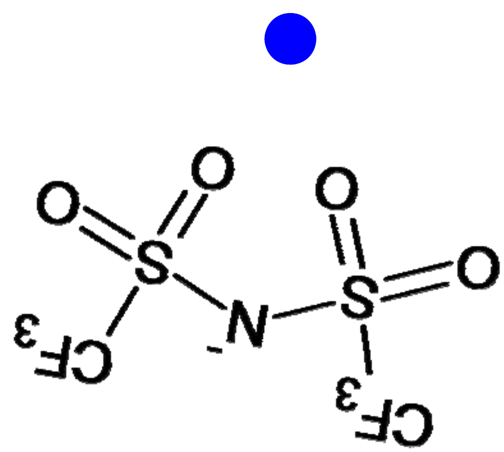


Pyr^+_{14}

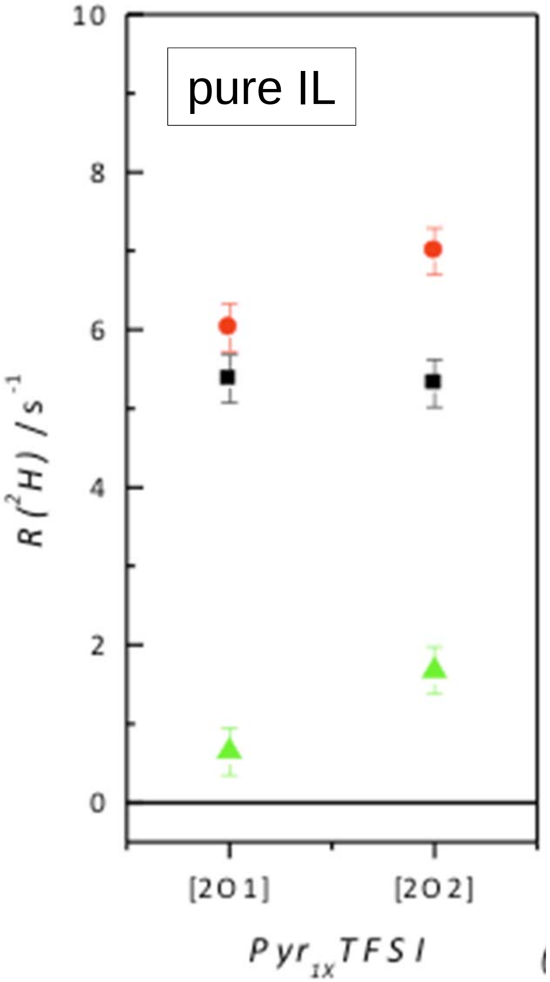


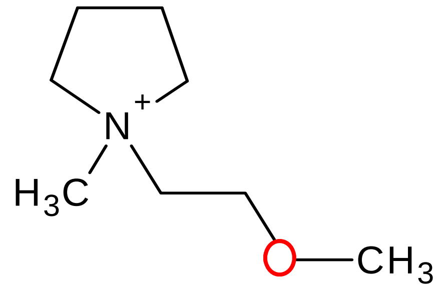
$Pyr^+_{1(2O1)}$





Cation aggregation in ILs with polar side chains





R_2 dependent on chain length in pure systems
⇨ slow local motions influenced

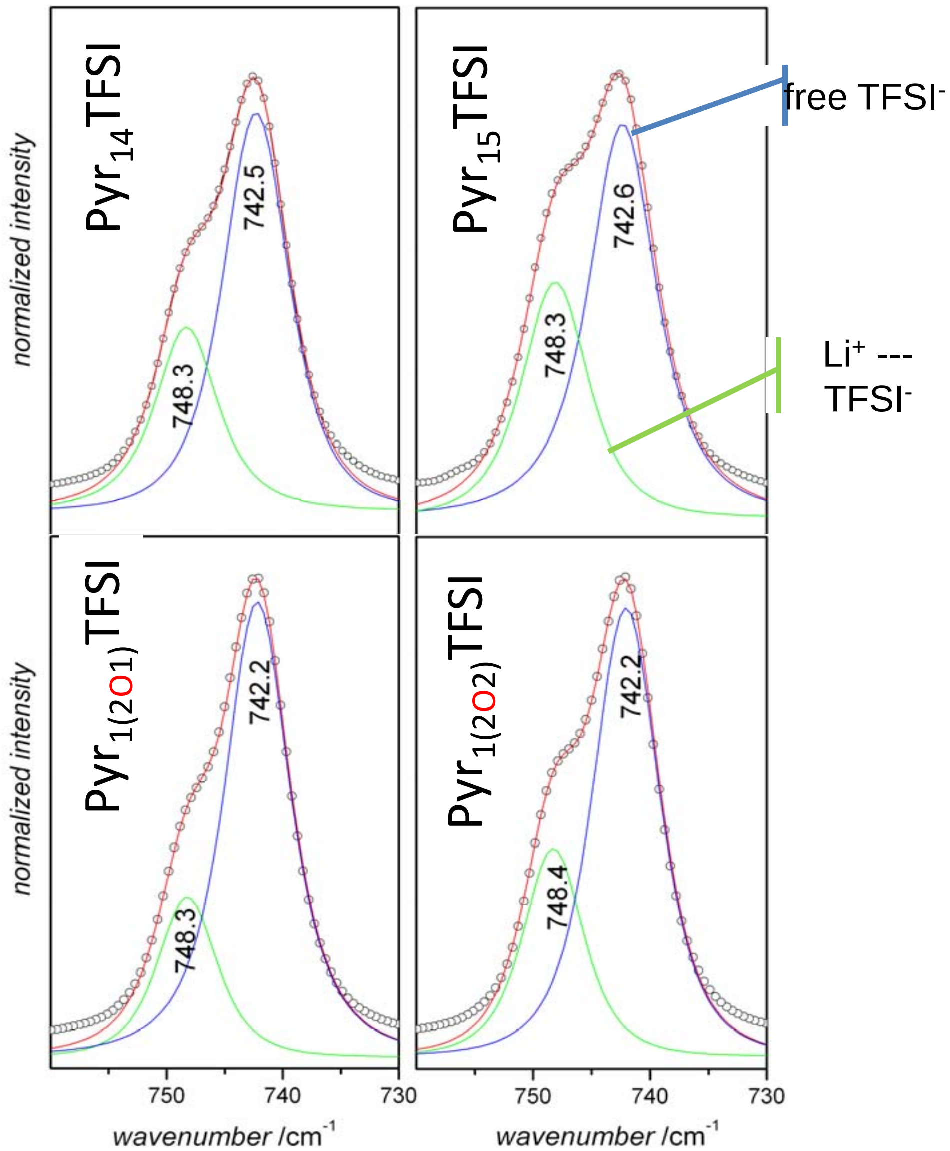
for systems with Li salt ΔR does

R_1 independent on chain length in pure systems
⇨ fast local motions not influenced

ΔR changes with chain length
⇨anisotropical arrangement

⇨aggregation of cations w/ polar group
⇨cations do not aggregate when a lithium salt is dissolved

PYR^{+}_{1A} – Li^{+} –$TFSI^{-}$ interactions

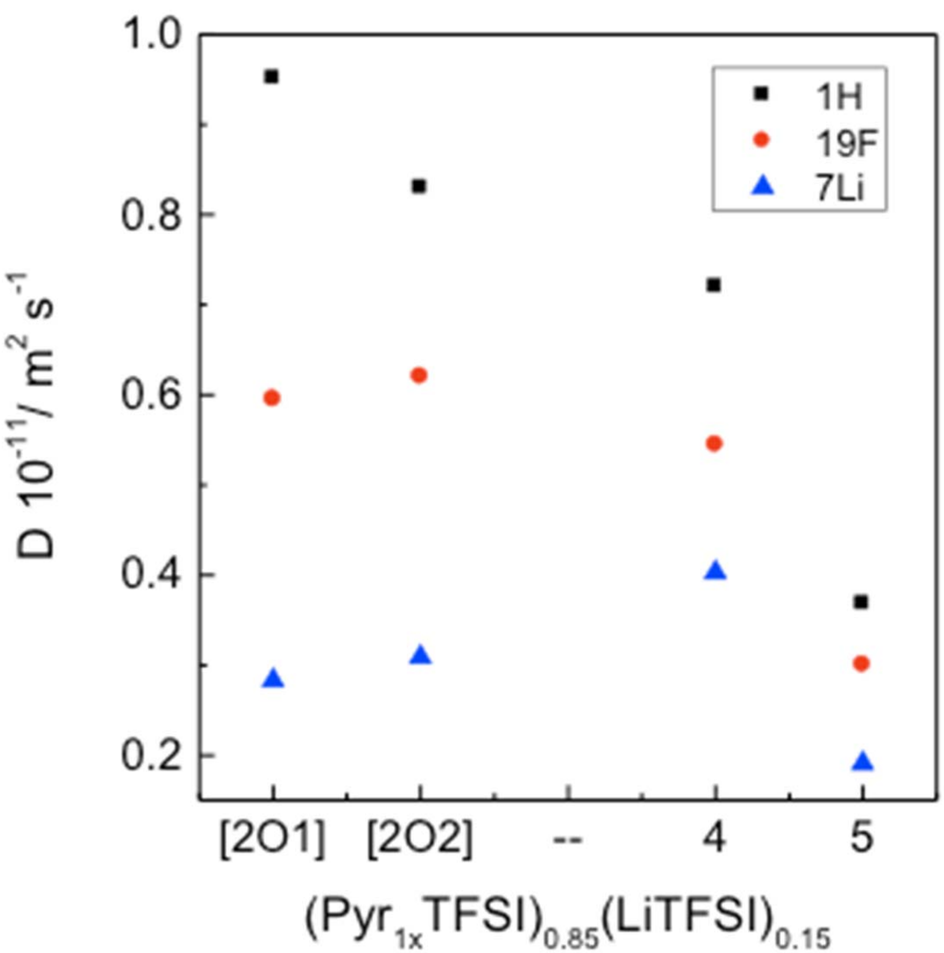


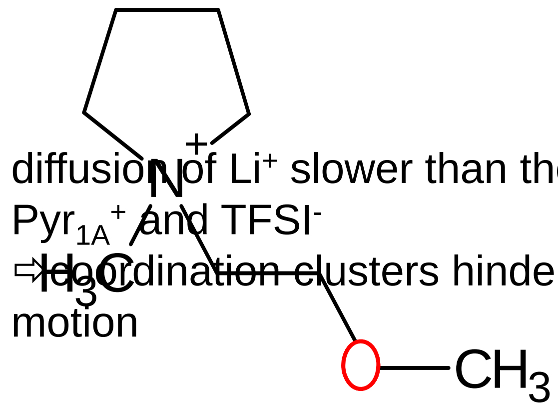
Raman

	n in Li···(TFSI)$_n$
$(Pyr_{14}TFSI)_{0.85}(LiTFSI)_{0.15}$	2.12
$(Pyr_{15}TFSI)_{0.85}(LiTFSI)_{0.15}$	2.34
$(Pyr_{1[2O1]}TFSI)_{0.85}(LiTFSI)_{0.15}$	1.55
$(Pyr_{1[2O2]}TFSI)_{0.85}(LiTFSI)_{0.15}$	1.87

Addition of oxygen into side chain reduces the number of TFSI anions in cluster.

Diffusion coefficient



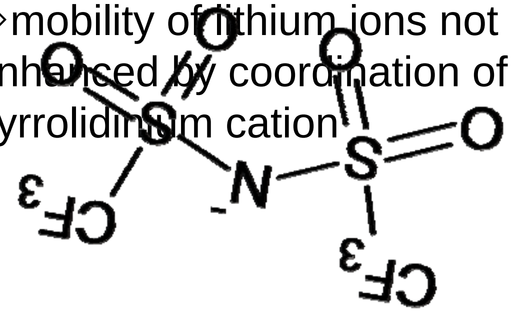


diffusion of Li^+ slower than those of Pyr_{1A}^+ and $TFSI^-$

⇨ coordination clusters hindered in motion

difference of diffusion coefficients larger for polar side chain than for non-polar side chain

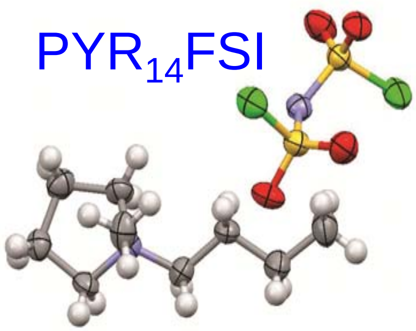
⇨ mobility of lithium ions not enhanced by coordination of pyrrolidinium cation



M. Kunze, et al., JPC C (2011)

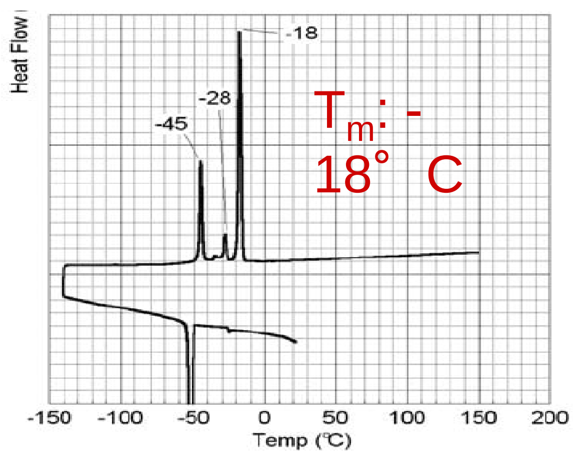
Tailored Ionic Liquid for Lithium Batteries

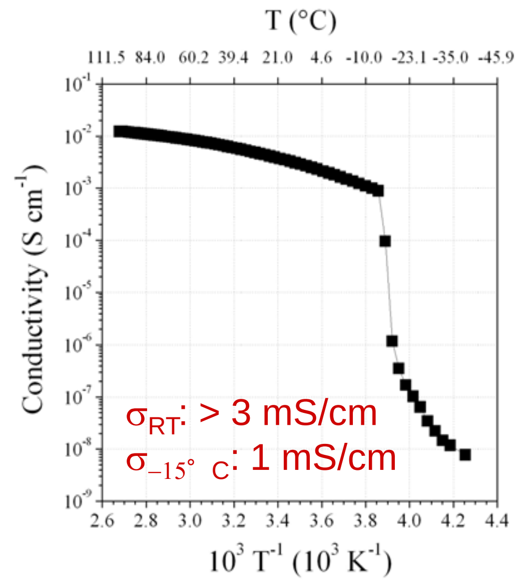
PYR$_{14}$FSI

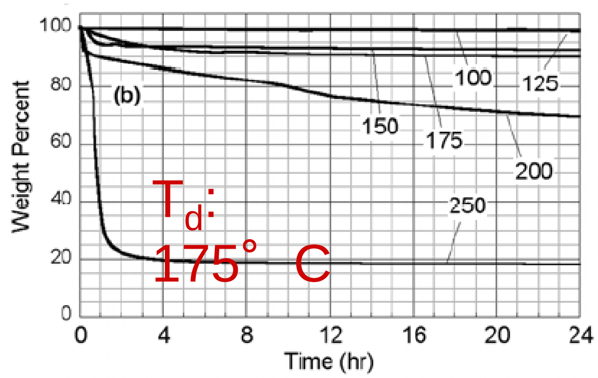


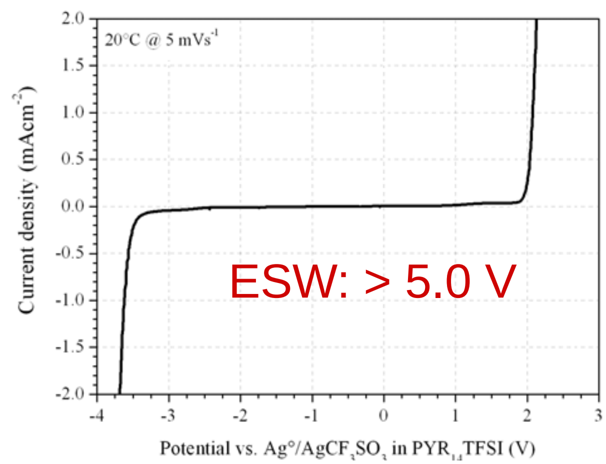
Purity > 99.5%

H_2O < 1ppm



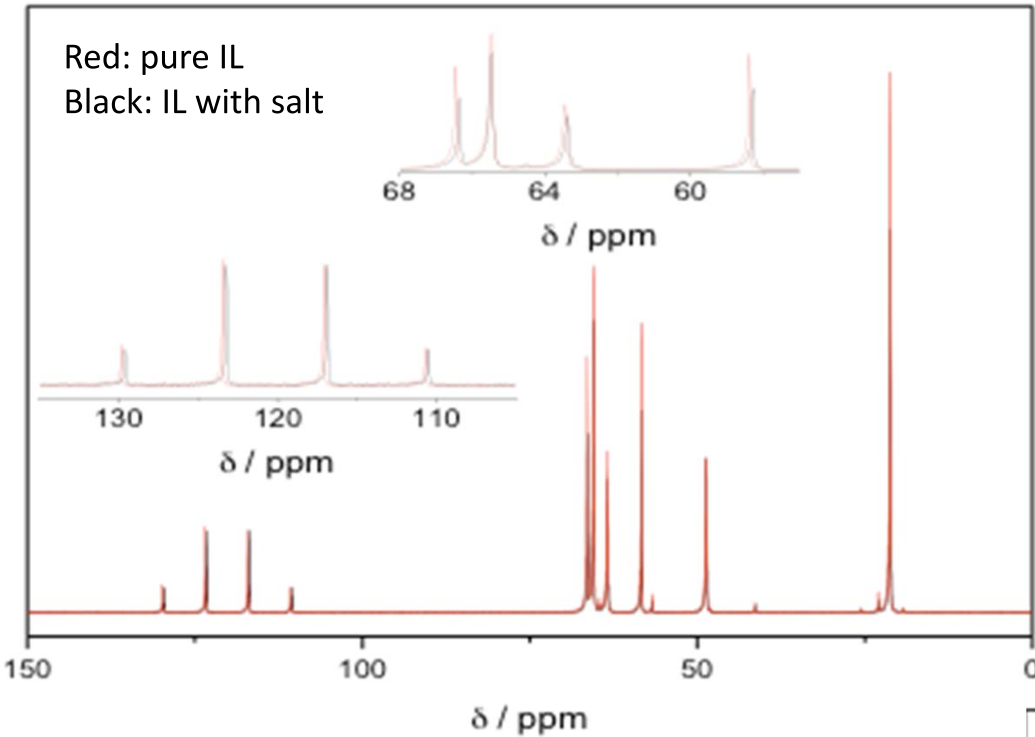


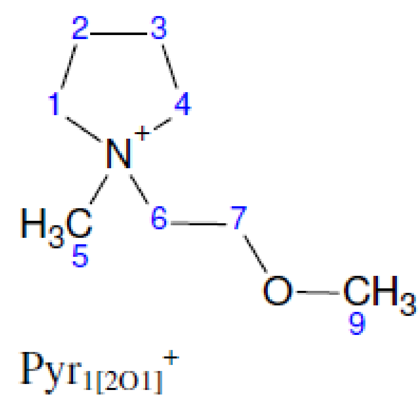




Paillard et al., JES 156, A891(2009), Kunze et al. JPC A 114, 1776 (2010)

Pyr^{+}_{14} – Li^{+} –$TFSI^{-}$ interactions





NMR-chemical shift

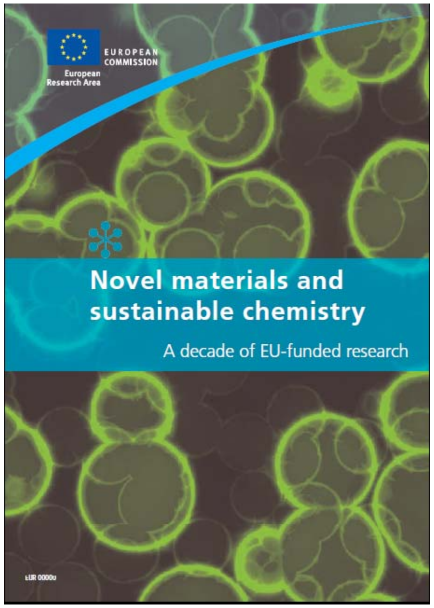
	pure	+ LiTFSI
δ / ppm	assignment (J^2(CH) = 2.5Hz)	Δδ / ppm (Hz)
58.377	C^9 (quadruplet)	-0.09 (-4.7)
63.447	C^6 (triplet)	-0.07 (-3.4)
65.479	C^1, C^4 (triplet)	-0.00 (-0.0)
66.454	C^7 (triplet)	-0.09 (-4.7)
120.271	$-CF_3$ (quadruplet, J^2(CF) =80.15Hz)	-0.23 (-11.7)

NMR features of oxygen neighbours are strongly affected as a result of the Li --- IL Cation interactions

ILLIBATT Project achievements

Demonstrated feasibility of Ionic Liquid-based batteries at the pre-industrial scale

ILLIBATT has been selected together with other most successful projects within the FP5 and FP6 calls
"Materials for a sustainable chemistry"
European Commission, Research Directorate-General
Directorate G-Industrial Technologies-Value-added Materials



A DECADE OF EU-FUNDED RESEARCH 21

Better, safer lithium batteries for everyday applications (2007-2009)

Solid-state Li-ion batteries set to deliver more power, last longer in phones, computers and cars.

Lithium ion batteries are excellent power sources for both small- and large-scale applications, from mobile phones and laptop computers to electric vehicles. However, they suffer from some drawbacks, such as age-related capacity loss and a tendency to overheat under continuous charge.

The ILLIBATT project is seeking to develop safer, better performing and environmentally benign technology that makes use of solid-state electrolytes containing non-volatile and thermally stable ionic liquids, together with nano-structured anodes and advanced cathodes. Resulting new materials are expected to be useful across an extended range of cell sizes, from micro-batteries to very large delocalised storage units (10-20kWh) and vehicle battery packs rated at up 50kWh.

The proposal for the three-year initiative identifies four key objectives:
- development of a green and safe solid-state electrolyte chemistry based on ionic liquids;
- use of novel nano-structured high capacity anodes prepared with the help of novel ionic liquids;
- investigation of the properties of the electrolytes and of their specific interactions with advanced commercial and self-prepared anode and cathode materials;
- construction of rechargeable lithium cells with optimised electrode and electrolyte components.

This research could position Europe at the forefront of a developing field of high performances batteries. This is a very important priority for European research considering the approaching paradigm change in the automotive industry towards hybrid cars powered by batteries and traditional fuel engines. The combination of innovations should make it possible to realise true solid-state lithium batteries operating at room temperature, delivering specific energy higher than 180 Wh/kg with respect to the overall weight of the cells. The coulombic efficiency is expected to average higher than 99 % during cycling; and lifetimes to reach 1 000 cycles with a 20 % maximum loss of capacity.

Project successes

By the end of the first project year, polymer electrolytes and an anhydrous high-purity ionic liquid exhibiting conductivity higher than 1 mS cm^{-1} had been prepared. The synthesis and characterisation of polymeric ionic liquids were also completed, together with a small-scale preparation of conducting composites containing suitable binder polymers and ionic liquids.

Electrochemical testing procedures and standardised conditions were defined, and samples of all the cathode materials have been tested.

In the remaining project period, work will continue with the design and fabrication of solvent-free, all-solid-state concept batteries, as well as evaluation of their electrochemical and safety performance.

Cu current collector
electrolyte
Li metal anode
composite cathode (between Al and electrolyte)
Al current collectors

The ILLIBAT Polymer Battery concept: a vacuum-sealed, laminated, solid-state cell and its voltage profile at 40 °C and different discharge rates.

Sub-ambient temperature ionic liquid (T_m = -18°C).

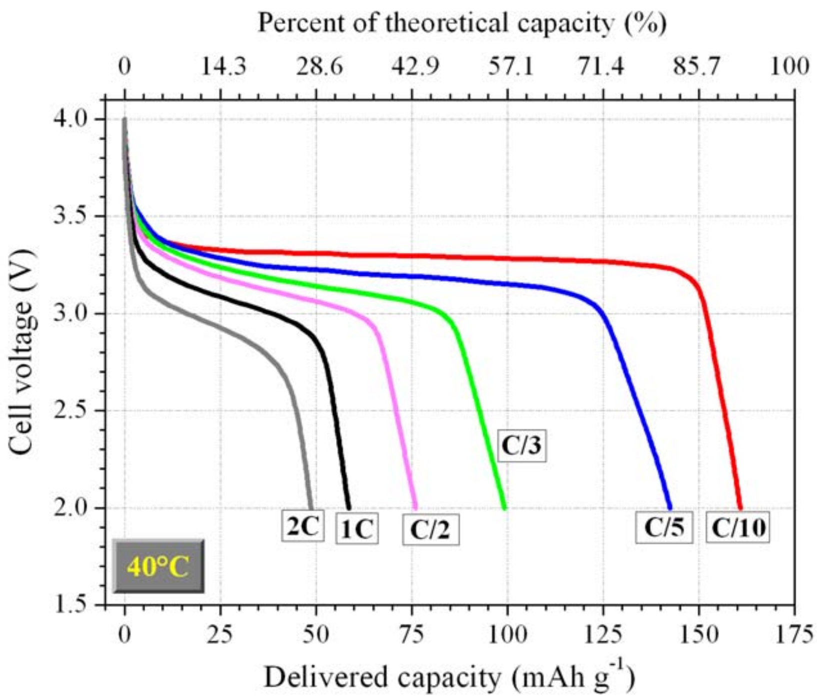
NMP3-CT-2006-033181 – ILLIBAT
Ionic liquid based lithium batteries
Total cost | € 2 667 513 – EC contribution | € 1 848 396
Project duration | January 2007 – December 2009 (36 months)
Coordinator | Martin Winter – Westfälische Wilhelms Universität Münster, Institute of Physical Chemistry, Münster, Germany. (former Technische Universitaet Graz, Institute for Chemistry and Technology of Inorganic Materials (ICTAS), Graz, Austria)

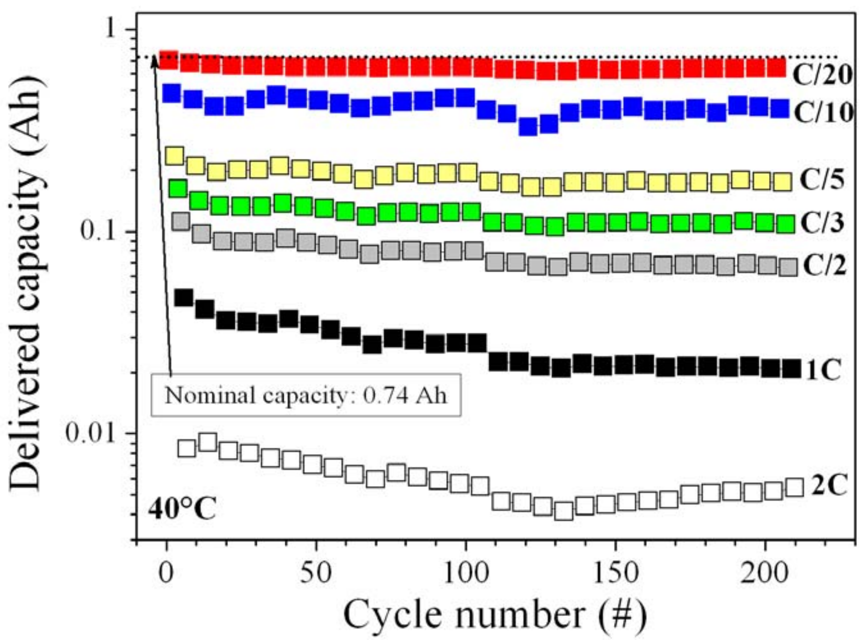
ILLIBATT Cells:

- Do not contain volatile components
- Halides are present only in the easy-to-recycle electrolyte
- All binders are halide-free

Battery tests: PEO-IL-LiX electrolyte (near RT tests)

Li / $P(EO)_{10}LiTFSI\text{-}PYR_{14}TFSI$ / $LiFePO_4$

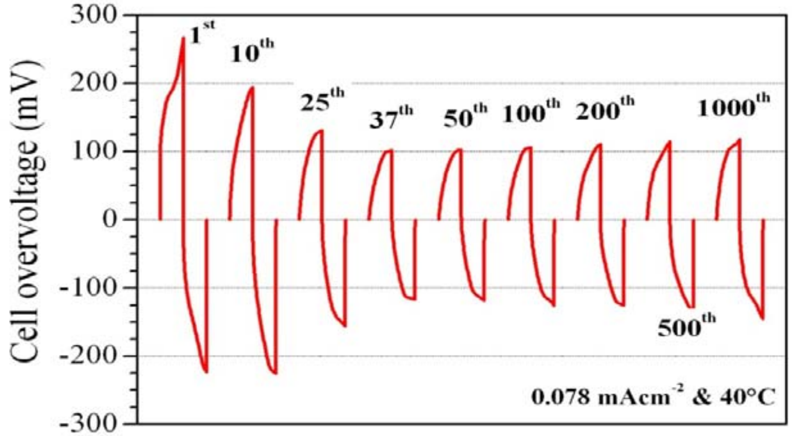


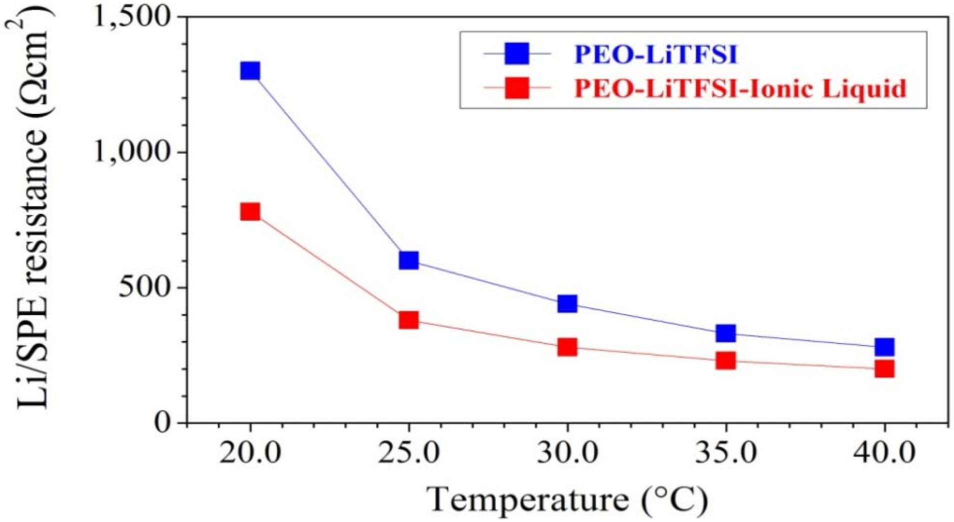


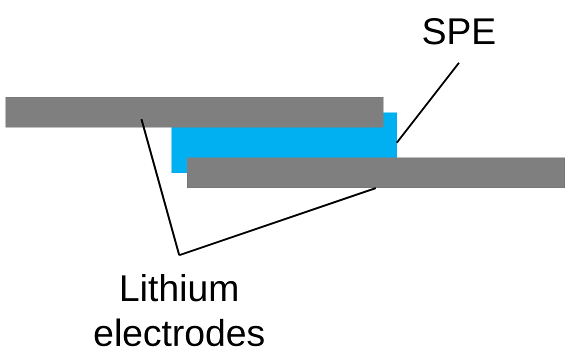
Large capacities (140 $mAhg^{-1}$) up to medium rates (C/5)
Moderate capacities (50-75 $mAhg^{-1}$) even at high rates (2C-1C)
> 90% of initial capacity is delivered upon about 200 cycles

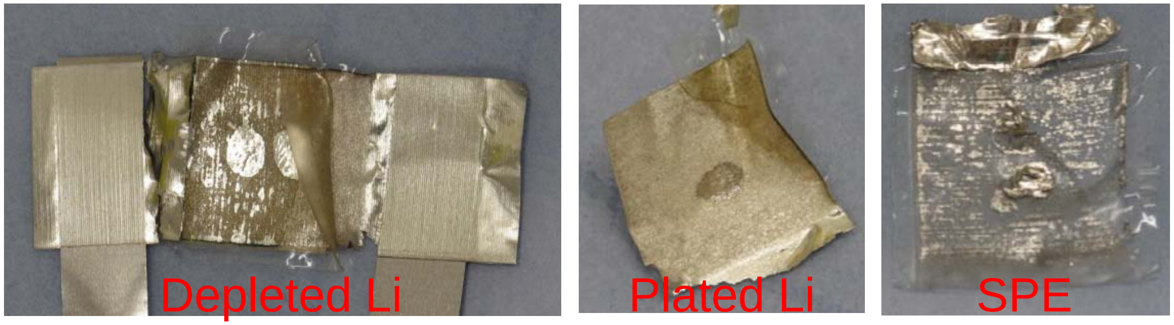
PEO-LiX-IL electrolytes: Li interface

PEO : LiTFSI : PYR_{14}TFSI = 20:2:4 (mol)









Excellent lithium plating/stripping performance
Lowered interface resistance